

TRANSACTIONS

of the
**American Society
for Steel Treating**

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RAY T. BAYLESS, *Editor*

Vol. XX

July, 1932

No. 1

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TRANSACTIONS

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PHOTOMICROGRAPHS AT LOW MAGNIFICATION

BY JAMES OSBORN LORD

Abstract

Apparatus and methods that may be used in making photomicrographs at magnifications ranging from one to twenty diameters are discussed. Three classifications of subject are considered.

First. Polished surfaces by vertical illumination. Here attention is directed principally toward the setup of apparatus in order to obtain uniform illumination.

Second. Rough surfaces of low relief. Here clear and natural portrayal of the object is considered.

Third. Rough surfaces, or objects, of high relief. This is chiefly a study of the geometrical principles of lenses to determine the limits of reducing the aperture of the lens to secure depth of focus and to aid in making the proper selection of objectives for the work at hand.

INTRODUCTION

THE trend of recently published treatises on metallography seems to be almost exclusively toward the development of technique in making photographs at increasingly high magnifications. The results have been extremely gratifying. The beautiful photomicrographs ranging in magnification from 2000 to over 5000 diameters that are found in the modern technical journals are somewhat dazzling to those who can appreciate the difficulties encountered in the wobbly equipment of a past decade. Even ultra-violet light is now being used with marvelous results, and structures are being resolved for visual interpretation that were considered hopelessly submicroscopic.

The author, James Osborn Lord, a member of the society, is assistant professor of metallurgy, Ohio State University, Columbus, Ohio. Manuscript received April 23, 1931.

On the other hand the vast majority of metallurgical photomicrographs for commercial use are taken at magnifications of less than five hundred diameters. With modern equipment these cause little difficulty down to about fifty diameters. The principles regarding them are the same as for higher powers but the application of these principles is simpler and requires less skill.

Little attention seems to have been paid to the range of magnification between one and twenty diameters. This range frequently proves baffling to the novice because the principles involved are quite different from those of the higher magnifications and most laboratories do not have the special equipment required for such work. The present article endeavors to list and explain some of the devices that can be used to obtain pleasing and faithful photomicrographs at magnifications less than twenty diameters. It is not confined to metallographic subjects but, in addition, deals with the type of thing that frequently confronts the plant metallographer:—fractures, fine-grained materials such as sands, small articles of various description, because every metallographer has to deal with such subjects on occasion and usually he spends more time with one of them than with a dozen photomicrographs of much higher magnification.

The differences in the principles involved, between low and high magnifications, may be summed up into differences in methods of illumination and differences in the use and behavior of lenses. These differences are more profound than might at first be imagined. The low power field is the border between photography and photomicrography and necessarily includes some of the elements of both. Illumination in the microscopic field is directed, intense, and the image is diagrammatic in nature and must be interpreted. In the photographic field the illumination is diffuse and general. The image is pictorial and self evident. It will be seen that, in low power micrographs, we have images that are sometimes pictorial and sometimes diagrammatic, and the illumination must meet the requirements of one condition or the other and, sometimes, of both.

The function of a microscopic lens is to make a highly magnified image of a carefully prepared, flat surface, and to resolve, in this image, the fine detail that occurs as markings on the surface. A photographic lens, on the other hand, must bring to a focus, on the same ground glass or plate, images of objects that are both near and far away. The ability of a lens to do this is termed its depth of focus. Depth of focus decreases rapidly as magnification increases,

and in low power work it is well to know the limits within which we can obtain satisfactory results.

APPARATUS

A number of devices are available, as attachments to the inverted, or horizontal, type of metallographic microscope, for taking low power pictures, and for the particular work for which they are de-

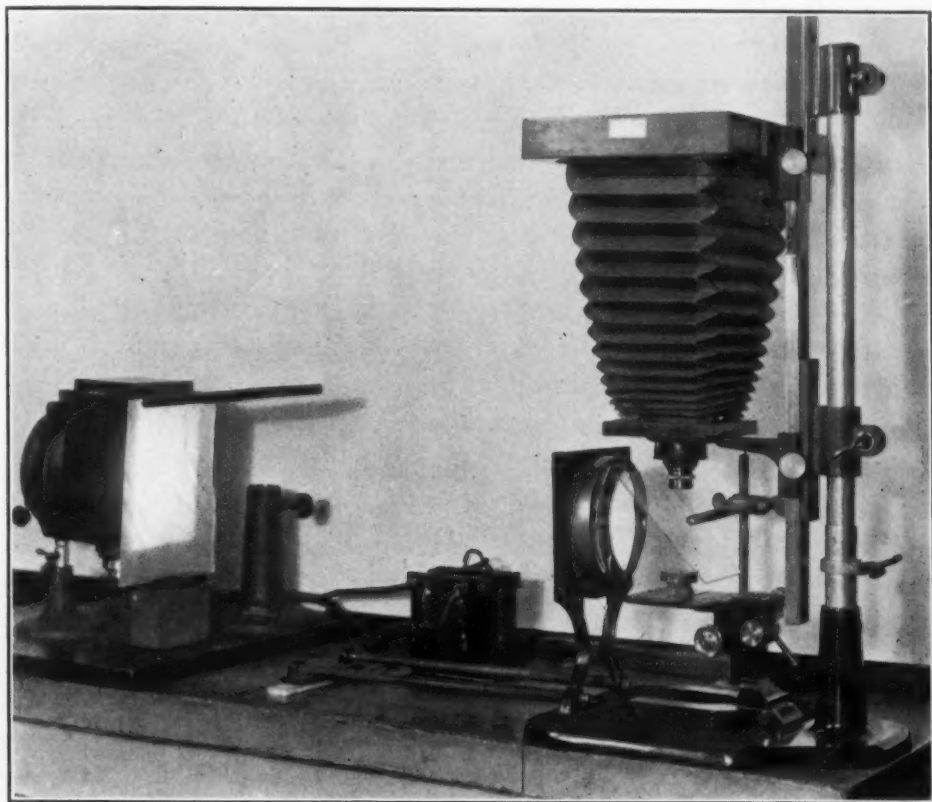


Fig. 1—Set-up of Apparatus for Low Power Photographs Known as Photomacrophs.

signed they are quite satisfactory. However, for general flexibility, the author prefers the vertical type of camera shown in Fig. 1 with 5x7 inch plate holders. Such cameras, of which there are several makes, are usually sold as student equipment.

The lenses should be of high grade, of the Tessar or Summar type, and range in focal length from about thirty millimeters to ten centimeters. Three such will be sufficient, say one 32 millimeters, one 64 millimeters, and one 10 centimeters. As will be explained later,

the iris diaphragms on these lenses have scarcely small enough openings, when in the closed position, to meet all situations, but this can be taken care of when necessary by using a diaphragm of black paper.

A stage with a rack and pinion, for adjusting the focus, is desirable though not essential as the focussing can be accomplished by sliding the front part of the camera on the support.

The illuminating lamp requires attention. It should be, as nearly as possible, a point source of light and very intense. The ribbon filament Mazda (6 volt) or a good carbon arc will do. At least two such lights should be available and be so mounted that they can be elevated to about eighteen inches if necessary. A focussing condenser should be attached to each light, the larger the condenser the better, and the adjustment be such that the rays can be focussed from parallel to rather abruptly converging toward the specimen. It is advisable to arrange the equipment so that the light can be used directly, without the focussing condenser.

A separate condenser should also be available as described later in the section relating to vertical illumination of polished surfaces. This condenser will have a rather short focus and should be at least 4 inches in diameter. Projection lantern condensers are satisfactory.

A plane glass reflector of considerable size will be needed. This is to be used in a manner similar to the plane glass illuminator of higher power work except that it will be placed between the lens and the object instead of above, or back of, the objective. It may be simply constructed by mounting a clean photographic plate, by its edge, in a burette clamp mounted on a ring stand. A supply of ground glasses and light filters should also be available. These and other minor necessities will be described under the particular section that treats of their use. A good focussing glass and a focussing cloth complete the list of requirements.

PHOTOGRAPHING OPAQUE POLISHED SURFACES

This is the type of work that is most familiar to the metallographer since all of the higher magnification work is done on polished metal surfaces with only the slight relief that is brought out by light etching. The essential requirement is vertical, or nearly vertical, illumination. This is best accomplished, for photographic purposes, in the case of high magnifications, by the plane glass illuminator, placed in the microscope tube above the objective.

The principle of reflection from a piece of plane glass can also be applied to low power work but the arrangement must be modified. Fig. 2 shows the arrangement for high power work. The beam of light AB is reflected by the plane glass $A'B'$ down through the objective which condenses it on the spot $A''B''$. It is reflected back into the objective, which has a short focus and wide aperture, and the image of $A''B''$ is focussed at $B'''A'''$. All the light incident upon $A''B''$ is reflected into the lens, hence $B'''A'''$ will be bright all over.

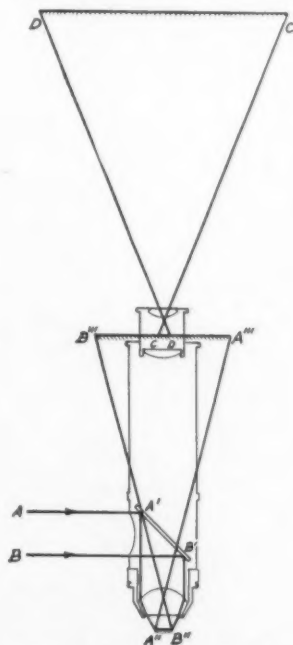


Fig. 2—Diagram Showing Arrangement of Reflector and Lenses for High Power Photomicrographic Work.

The eyepiece examines only the small portion of the total area whose diameter is shown at CD . This will be quite uniformly illuminated.

The requisites in the above case are that the diameter of the opening in the objective be large compared to the area of the specimen observed, and that the magnification be reasonably high. The limiting arrangement seems to be obtained in the case of a 16 millimeter objective without an eyepiece. This usually gives an image that is bright in the center but dark at the edges.

Fig. 3 shows what will happen if we try this with low magnification. The spot DG is focussed at gE and is bright, but the remainder of the image is dark, since the portion of the object that it represents reflects no light into the objective.

Assuming light rays that are parallel from the source, the plane glass reflector can be made to illuminate the surface vertically as shown in Fig. 4, but if the area to be examined is larger than the

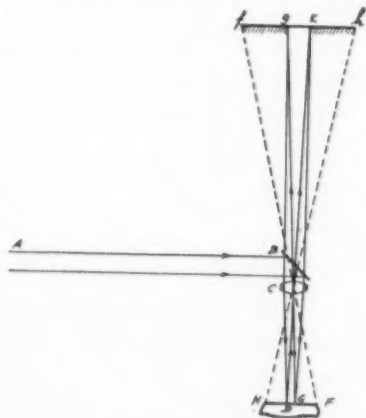


Fig. 3 — Diagram Showing What Happens if the Same Arrangement in Fig. 2 is Applied to Lower Power Work.

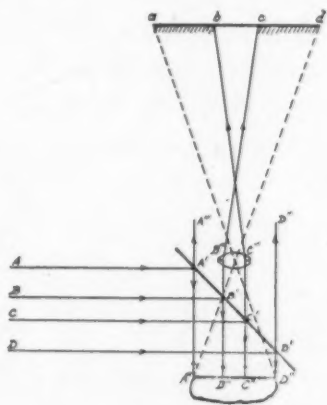


Fig. 4—Diagram Showing Set-up Used in Obtaining Photomicrograph Shown in Fig. 6.

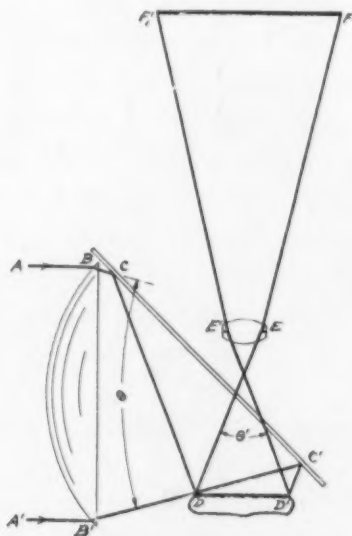


Fig. 5 — Diagram Showing Set-up Used in Obtaining Photomicrograph Shown in Fig. 7.

effective opening of the lens $B'''C'''$ the edges will be dark. Fig. 6 shows the result on a specimen so illuminated.

In order, therefore, to illuminate, uniformly, a specimen that is larger than the lens itself it will be necessary to bring the light onto it in such a manner that all rays will be reflected into the objective. An arrangement for doing this is shown diagrammatically in Fig. 5.

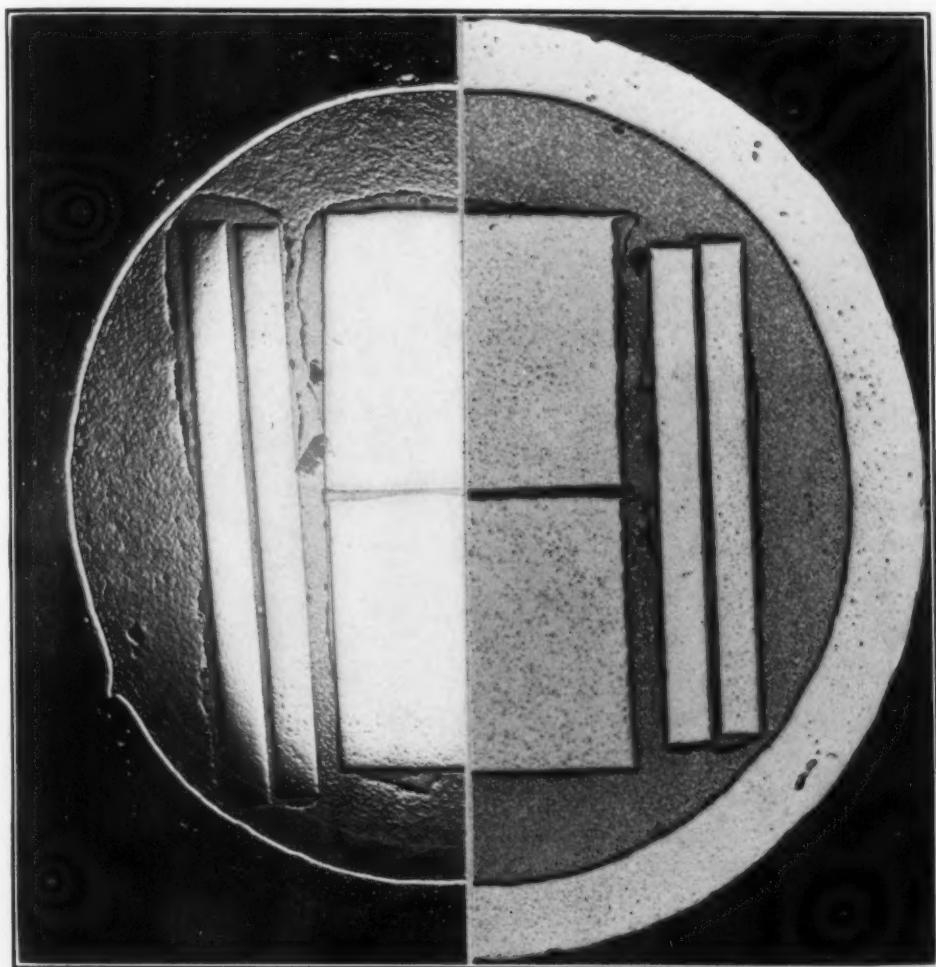


Fig. 6 (Left)—Sheet Steel Specimens Mounted in Low Melting Alloy Made by Using Incorrect Illumination Shown Diagrammatically in Fig. 4. Fig. 7—Same Specimens as in Fig. 6 Using Correct Illuminating Shown Diagrammatically in Fig. 5. $\times 4.3$

A wide beam of light AA' is converged by the condenser BB' to form a pencil of rays which has at least as great an angle as that formed by lines drawn from the limits of the surface of the object to the opposite sides of the opening in the objective. This pencil of rays is reflected by the plane glass CC' onto the object whence it is reflected by the polished surface up into the lens $E'E$ and focussed at $F'F$. Fig. 7 shows the result of such illumination on the same specimen as that used in Fig. 6 and Fig. 1 shows the actual set-up of equipment that was used. The ground glass is used in front of the light source as an added measure to insure freedom from unevenness in illumination, but the field was apparently uniform before the ground glass was put in.

A few points of instruction should be given regarding the care in setting up the apparatus. Best and quickest results are secured by nicety in placing the parts. The source of light and the center of the condenser should be on the same horizontal line. As stated above, the pencil of rays from the condenser should make about the same angle as the lines drawn from opposite sides of the object surface to the opposite sides of the objective opening. That is, referring to Fig. 5 angle Θ should equal angle Θ' . This is accomplished by varying the distance between the source of light and the condenser. The single condenser is shown in the cut, but with a short focus objective such as the 32 millimeter the double condenser will be necessary. The reflector CC' will be at exactly 45 degrees and nearly touching the top of the condenser. The object is placed squarely in the center of the spot of light and raised until it just misses the lower edge of the beam of light $B'C'$. The focussing should be done by moving the objective rather than the stage. The set-up should be made without a ground glass in front of the light source and adjustments made until the image on the ground glass of the camera is uniformly illuminated, or nearly so. If it is necessary to stop down the lens to secure a perfectly flat field it will be found that dark spots appear on the image, requiring still greater care in adjusting the illumination. With good lenses it should be possible to use them nearly wide open, and they should be so used for this type of work.

Any reduction in quantity of light should be made by interposing extra ground glasses or perhaps color filters between the light source and the condenser. It will be found that a ground glass near the condenser reduces the illumination much more than it does near the light source; hence the intensity of illumination may be varied between limits by changing the position of this ground glass. With the Mazda light and the above set-up, most exposures on ordinary plates will be greater than one second, so there would be no object in reducing the intensity of illumination.

The author has spent many hours trying other methods of illumination for this purpose with only unsatisfactory results. Attempts to use various diffusion devices to take the place of the condenser all meet with failure and no method of side illumination is adequate.

The above method will give satisfactory results on polished surfaces and on lightly etched surfaces. Figs. 8, 9, and 10 show applica-

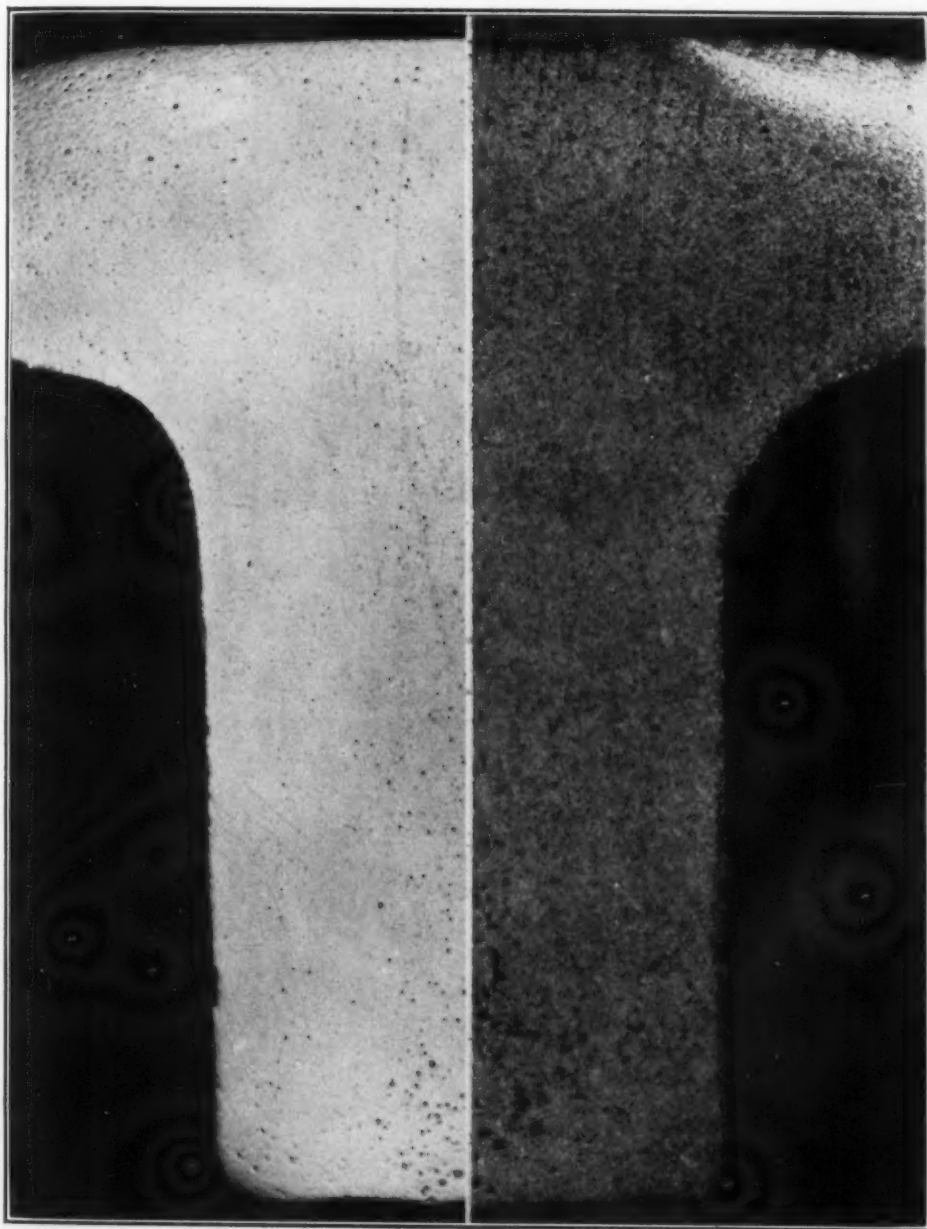


Fig. 8 (Left)—Polished Section of Forging. Fig. 9 (Right)—Same Specimen as Fig. 8 Etched to Show Segregation. Light Areas Show Heat Treatment, Other Parts Do Not. $\times 5$.

tions. Note particularly the necessity for even illumination in Fig. 9, where slight irregularities would easily obscure the feature to be elucidated, namely, the small white streaks of hardened metal indicating uneven and incomplete heating.

ROUGH SURFACES OF LOW RELIEF

This includes deep etched or pickled surfaces; roughly ground surfaces, square fractures of low relief, certain types of electro deposits and the like.

The illumination of such objects is not as a rule difficult. Oblique lighting from one side usually is satisfactory. Vertical illumination is entirely unsatisfactory for such work because it either makes the surface appear flat or resolves it into an unintelligible array of bright points of light due to the fact that only the flat tops and bottoms of the surface irregularities reflect such light into the objective.

The degree of contrast in the image may be controlled by raising or lowering the light: the higher the light, the more nearly vertical the rays, the lower the contrast. This can be still further lowered by using two lights from different directions. Diffusing ground glasses should, in all events, be used in front of the lights. The degree of contrast desired will depend upon the specimen and the purpose of the photograph. Usually the aim will be to simulate the appearance of the specimen as seen visually in diffuse but directed light, such as would be obtained near a window. In the case of fractures, especially fresh ones that are not tarnished, it will be necessary to suppress contrast considerably. Particularly will it be necessary to have the light as diffused as possible to cut down the effect of bright reflections from the crystal facets if the grains are coarse.

Deeply pickled surfaces present an interesting problem, especially if the surface is perpendicular to rolling or forging direction. Here the normal surface is rough and picked up. Segregated material or defects of various kinds produce a secondary structure impressed on this erstwhile rough surface. To show this secondary structure best it is advantageous to suppress the rough appearance of the normal pickled structure as much as possible. To do this, two lights are used, placed rather low, and illuminating the specimen in opposite directions.

Another point to be considered in relation to this type of photograph is the optical illusion, often observed, where the relief becomes reversed, and the high points seem low and vice versa. This is very troublesome at times and is not always easy to correct. Wherever possible, some feature in the photograph should give positive evidence of the proper orientation. Some deep cut, hole, or knob, that is unmistakable, will help. In higher power work, polishing scratches

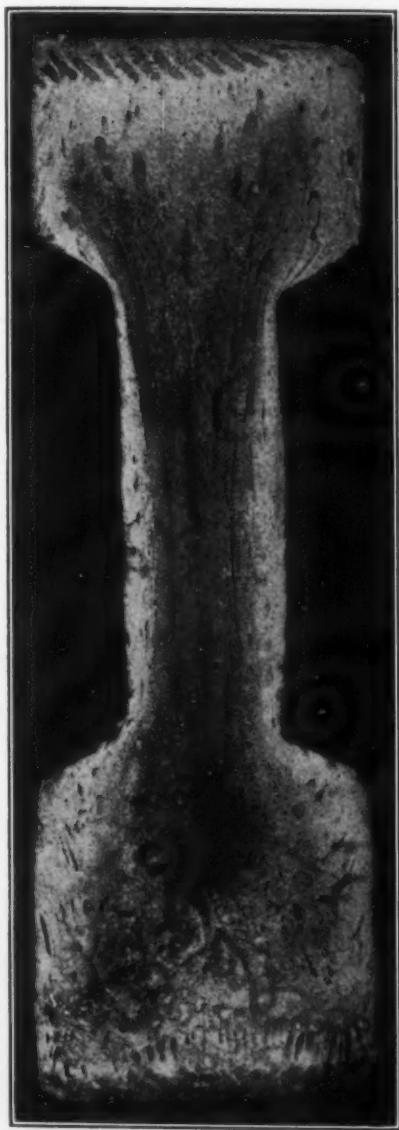


Fig. 10—Specimen Showing Segregation After Etching in Nital. Method of Fig. 5 Used. $\times 3$.

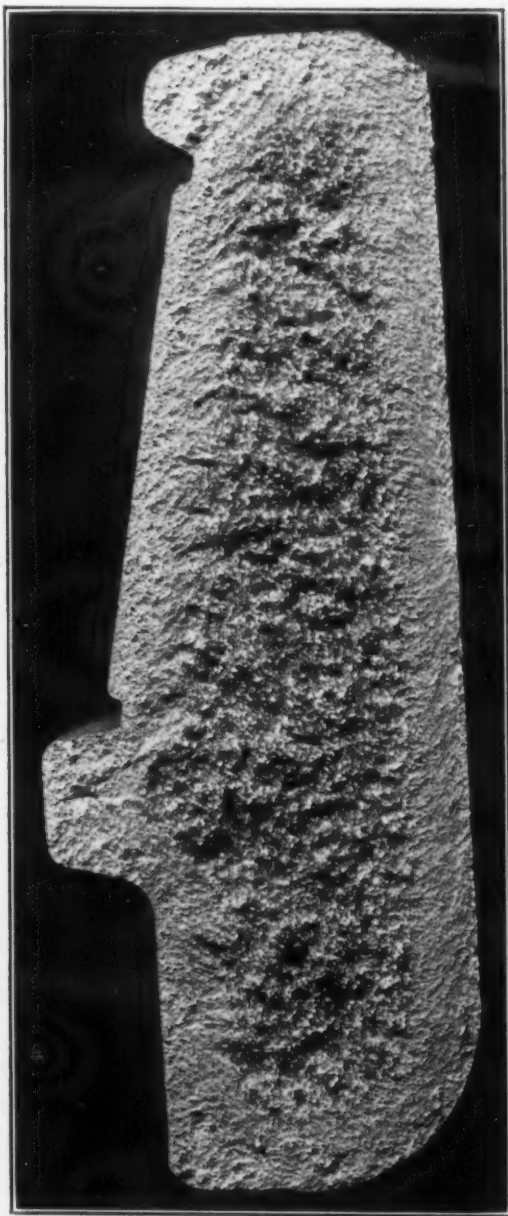


Fig. 11—Fracture of Carburized Bearing Cone. $\times 5$.

usually serve the purpose. The illumination may vary in intensity from one side of the object to the other so as to give definite indication of its principal direction. The final photograph should always be mounted so that the direction of illumination is from the left and above. The method of focussing sometimes solves the problem. This should be done so that the center portion of the specimen and the

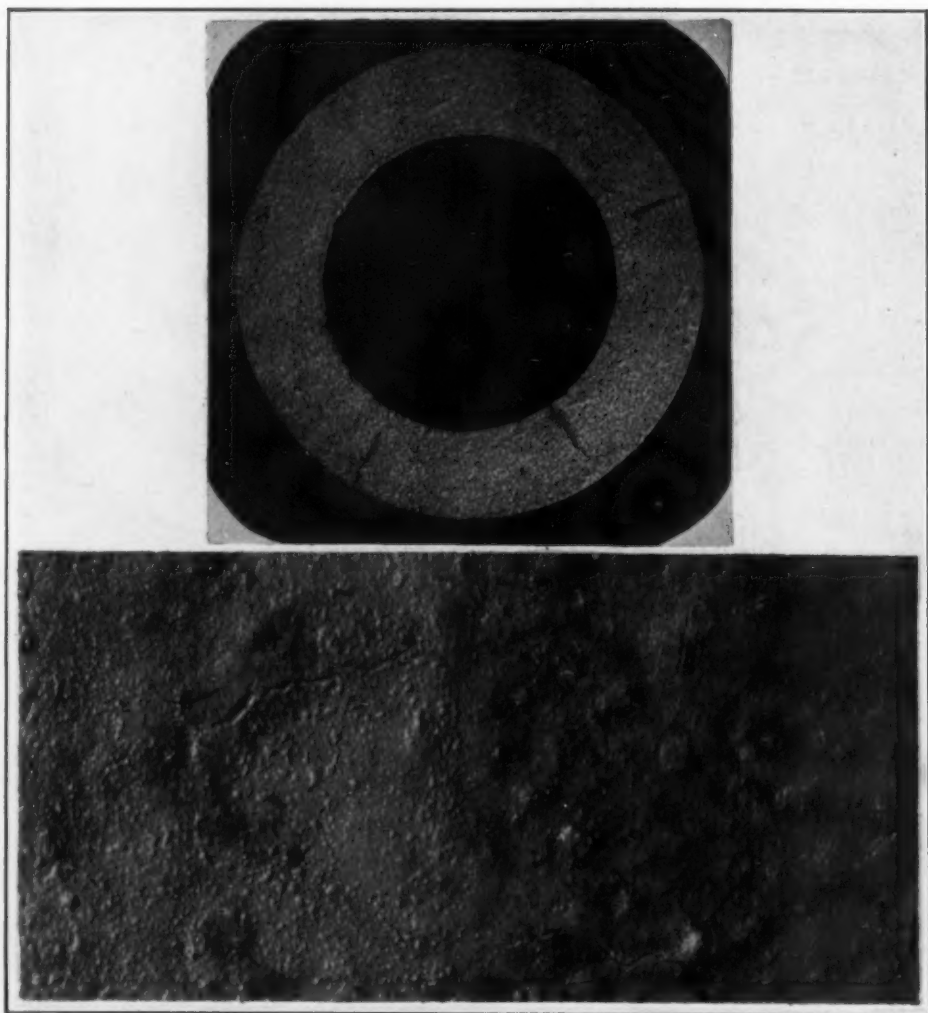


Fig. 12 (Upper)—Section of Cold Drawn Tube Deep Pickled in Hydrochloric Acid, Showing Cracks. $\times 2$. Fig. 13 (Lower)—Surface of Hard Burned Brick Showing Effect of Heat Treatment on Left Portion. $\times 6$.

highest points are in sharp focus. If the lens has a reasonably wide aperture the deeper portions may be left slightly blurred; not sufficiently, however, to obscure any appreciable detail. Several examples of this kind of work are given in Figs. 11 to 13, inclusive.

ARTICLES OF HIGH RELIEF

This classification includes rough fractures, cavities, small articles of a discrete nature such as crystals and fragments, sands, very small manufactured articles such as jewelry or dental objects.

Most of the remarks about illumination in the preceding section

apply equally well to this kind of work. Many special cases arise, however, and the more important of these will be dealt with at the close of this section.

It will be found that the subject of depth of focus is the principal stumbling block in obtaining pictures of this kind. By depth of focus we mean the ability of a lens to bring to a satisfactorily sharp focus on the photographic plate, objects that are both near and far away. A camera lens of small aperture is said to have great depth of focus while one of wide aperture will have little depth of focus unless, perchance, it is a very small camera.

While depth can be easily controlled in the case of ordinary camera work by simply reducing the size of the aperture by stopping down the lens, the problem becomes quite complicated where the image is magnified. This is due to the fact that there is a very definite limit to the amount of stopping down that is permissible. This limit depends upon the magnification. To understand why this limit exists and to be able to estimate it in actual situations we must refer to some of the physical and geometrical properties of lenses.

RESOLVING POWER AND NUMERICAL APERTURE

Consider a simple lens which is focussed on a brightly illuminated object of such small dimensions that it can be considered a geometrical point within all limits of possible magnification.¹ Imagine that the image of this point is sharply focussed on the ground glass of the camera. Now, no matter how carefully the focussing is done, it will be found, if the image is examined with a focussing glass of sufficient magnification, that this image is not a point but a disk. If we examine it still more carefully we will find that the disk has faint concentric rings around it.

This phenomenon is due to the manner in which light is refracted and transmitted by lenses. It has nothing to do with the accuracy with which the lenses are ground or the focussing done, but depends directly on the wave length of the light and inversely on the size of the opening in the lens, i. e., the aperture.

If the object consists of a number of such points and they are placed so close together that their disk images overlap, it is evident

¹In working out the calculations and derivations that follow reference is made to the article entitled "Optics of Metallography" by W. L. Patterson, *TRANSACTIONS, American Society for Steel Treating*, Nov. 1921, pages 108 to 132, and also the same article with slight changes in "The Metallography and Heat Treatment of Iron and Steel" by Albert Sauveur.

that no amount of magnification will show them as separate images, because the lens will not resolve them. If, instead of points, we use finely ruled lines spaced at equal distances side by side, the ability of the lens to make separate images of these lines will be a measure of its resolving power. By definition resolving power equals the num-

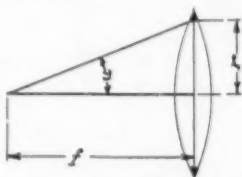


Fig. 14 — Diagram Illustrating What is Known as Numerical Aperture.

ber of lines per unit of length of which a lens can make separate images. Resolving power, however, has nothing to do with magnification. In order to see the images of the lines we usually magnify them, but whether or not they are present as separate images depends only upon the properties mentioned above.

Abbe found that resolving power was directly proportional to a characteristic of the lens which he called "numerical aperture." Referring to the diagram Fig. 14:—

$$\text{Numerical Aperture (N.A.)} = n \sin u. \quad (1)$$

n = the index of refraction of the medium between the lens and the object.

u = $\frac{1}{2}$ the angle subtended by the effective aperture² of the lens from a point on the object.

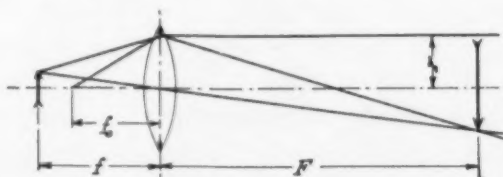


Fig. 15—Diagram Illustrating Numerical Aperture and Magnification.

If now, we let λ represent the wave length of the light used, we may write:

$$\text{Resolving Power} = 2 \frac{\text{N.A.}}{\lambda}$$

²The aperture of a lens is the diameter of the opening through which the light passes. This can be controlled by the use of diaphragms. It will be seen that "numerical aperture" and "aperture" are not the same thing.

The unit of length by which resolving power is measured is the same as that by which λ is measured. The micron ($\mu = 0.001$ millimeters) is a convenient unit.

For low power lenses of relatively small aperture and large focal length, and with air between the lens and object, we may approximate equation (1) by:

$$\text{N.A.} = \tan u, \quad (\text{instead of } 1 \sin u).$$

or, referring to Fig. 14,

$$\text{N.A.} = \frac{r}{f}; \quad \text{where } u \text{ is small.} \quad (2)$$

NUMERICAL APERTURE AND MAGNIFICATION

Let us consider the set-up represented diagrammatically in Fig. 15.

Let f_0 represent the rated focal length of the objective. (With the lens placed so that the distance between its optical center and an object is f_0 , the image will be at an infinite distance.)

Let f = the actual distance from the lens to object. In this position the image is assumed to be at distance F on the other side of the lens.^a

Let M = the magnification, i. e., diameter of image divided by diameter of object.

It is easy to show (see appendix I) that

$$f = f_0 \left(\frac{M + 1}{M} \right).$$

Substituting in our formula (II) for N.A.:

$$\text{N.A.} = \frac{rM}{f_0 (M + 1)};$$

r being the radius of the aperture.

Therefore;

$$\text{N.A.} = \frac{1}{2} \cdot \frac{\text{diameter of aperture}}{f_0} \cdot \frac{M}{M + 1}$$

Instead of using diameter of aperture, we may follow camera practice and rate the aperture according to the F system, which states that:—

^aThe symbols used for focal distances, here and in the appendix, are not the same as those found in elementary texts in physics, the reason being that the author felt that they would be somewhat confusing to all except those already familiar with such derivations. To translate these symbols to the customary ones the substitutions; $f = p$ and $F = q$ are evident.

Aperture (F system) = rated focal length divided by the diameter of aperture.

$$= \frac{f_o}{\text{Diam. of aperture}}$$

So, letting F be the aperture by the F system;

$$\text{N.A.} = \frac{1}{2F} \frac{M}{M+1} \quad (3)$$

RESOLVING POWER AND MAGNIFICATION

It is evident, from what has been said thus far, that the extent to which a photograph is blurred depends upon the size of the disk image which the lens makes of a point upon which it is focussed. The diameter of this disk image will be referred to as the diameter of the focal spot when measured at a magnification of unity, i. e., when the image and object are equidistant from the lens. The diameter of the focal spot may be defined as the reciprocal of resolving power so that, representing its value by d ;

$$d = \frac{1}{\text{resolving power}} = \frac{\lambda}{2 \text{ N.A.}}$$

If λ is expressed in microns and d is in millimeters:—

$$d = \frac{0.001\lambda}{2 \text{ N.A.}} = \frac{0.0005\lambda}{\text{N.A.}} = 0.001 F \frac{(M+1)}{M} \lambda$$

For yellow light $\lambda = 0.5\mu$ (about) then

$$d = 0.0005 F \left(\frac{M+1}{M} \right) \quad (4)$$

LIMITING APERTURE AND MAGNIFICATION

If we represent the limit of visibility by V (i. e. V is the diameter of the smallest visible feature in the image) we may write:

$$p = \frac{V}{M}$$

Where p is the diameter of the smallest particle in the object which must be resolved, in the image, for ordinary vision. For maximum visual resolution, d (above) should not exceed p , and equating:—

$$0.0005 F \left(\frac{M+1}{M} \right) = \frac{V}{M}$$

whence:—

$$F = \frac{V}{0.0005 (M + 1)} = \frac{2000 V}{M + 1}$$

Now if we were actually examining the image of a point we would have to make V as small as $1/20$ millimeter, since we could distinguish it as a disk if it were larger than that. For pictorial work, however, where the image is composed of modulated surfaces, edges, lights and shadows; and a pleasing appearance with the general effect of sharp focus is desired, it will be found that V can be made as large as 0.3 millimeters with no noticeable blurring. Substituting then in the above equation, we get:

$$F = \frac{600}{M + 1} \quad (5)$$

As an example, suppose that we want to photograph a rough surface at fifteen diameters. The contour of the surface is such that the smallest possible aperture must be used in the lens. Applying the above formula:—

$$F = \frac{600}{15 + 1} = 37.5$$

A smaller aperture than $F/37.5$ would only reduce the definition over the whole picture. With a 32 millimeter objective the actual diameter of aperture would be $32/37.5 = 0.85$ millimeters.

DEPTH OF FOCUS AND DEFINITION

It is desirable to carry our calculations farther and determine the limits of magnification and definition for very rough surfaces or

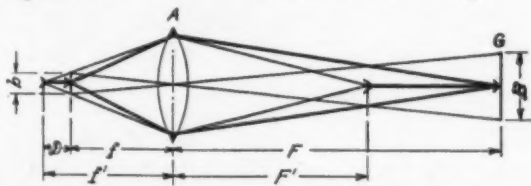


Fig. 16—Diagram Illustrating Depth of Focus and Definition.

for small objects like crystals, where it is necessary to have all parts in focus. We may represent this condition by Fig. 16 where the lens at A makes an image of the tip of the arrow at G. The arrow is placed perpendicular to the lens and its length is representative of

the degree of unevenness of the object to be photographed. The length D then, is the "depth of focus." The image of the remainder of the arrow lies in the space to the left of G , as shown, and the focal distances from the lens to the fronts and backs of object and image are, in order, f ; f^1 ; F ; F^1 .

We may show (Appendix II) that:

$$D = f^1 - f = \frac{F - F^1}{MM^1}$$

Where MM^1 is the product of the magnifications at the two ends of the image. Writing this another way:

$$F - F^1 = MM^1 D$$

The depth of the image, in space, is equal to the depth of the object (i. e. depth of focus) times the product of the magnifications at the two ends of the image.

This explains why, in ordinary camera work, where the magnifications are fractional (less than one), no great difficulty is experienced in obtaining a sharp focus for near and far objects on the same plate. As the object recedes, MM^1 diminishes rapidly and soon becomes negligible. Where the magnification is greater than one, as in microscopic work, the opposite effect occurs, and the depth of the image increases with a rapidity almost equal to the square of the magnification. For very high power work, even the slight differences in focal distance caused by light etching of the polished surface of the object are sufficient to throw some of the features out of focus. Hence the necessity for careful polishing and very light etching noted in recent works on this subject. In the field of low magnifications, we can take care of a limited variation of focal distance.

As explained earlier in this paper, the best focus should be on the portion of the object nearest the lens. For this the ground glass will be placed at G (Fig. 16), where the point of the arrow is in true focus. If, now, we let b equal the diameter of the right circular section, at distance f from the lens (at the tip of the arrow), of the cone of rays formed by the lens and a point at the tail of the arrow (distance f^1), the image of this circular section, at the major focus F (i. e. on the ground glass), will be the magnification at F times b . or:

$$B = Mb.$$

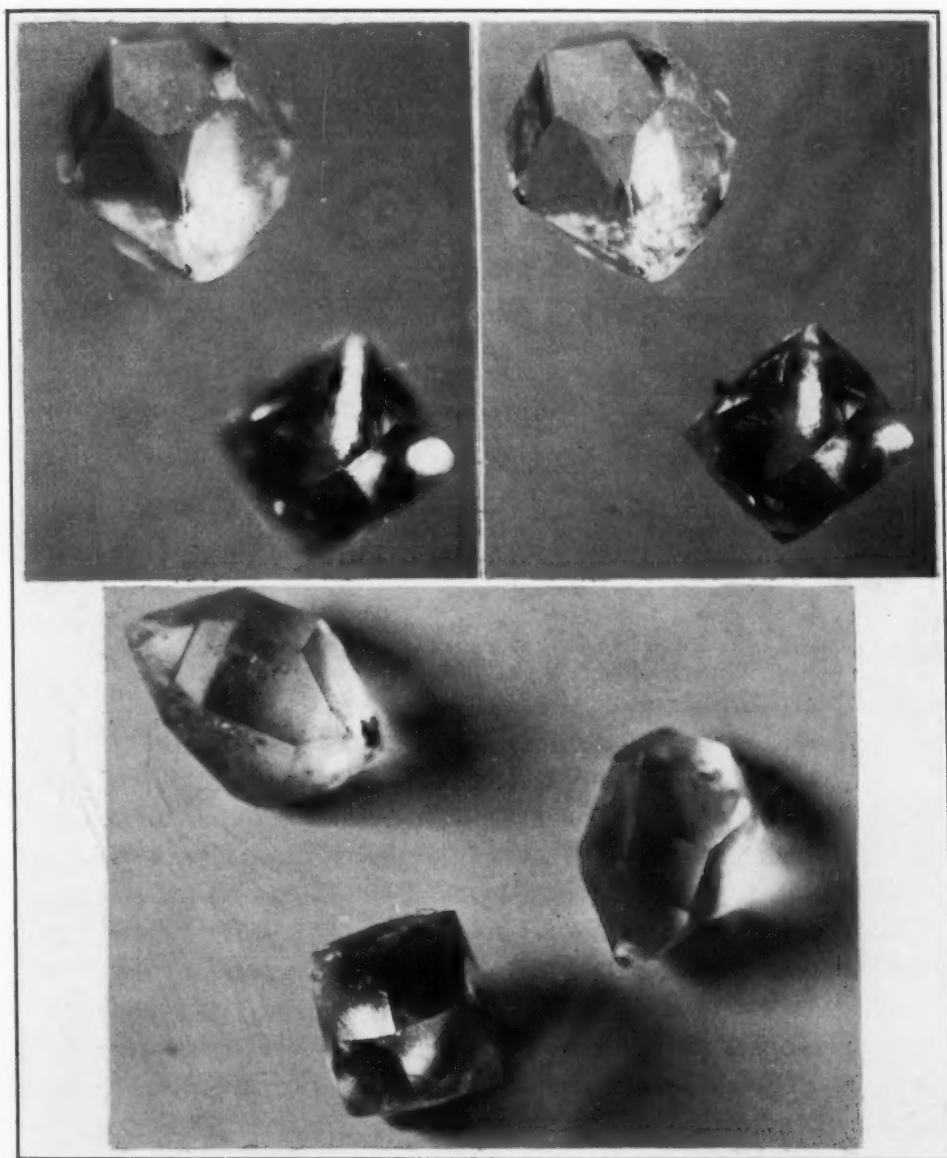


Fig. 17 (Left)—Photomicrograph Illustrating the Effect of Stopping Down the Aperture to Sharpen the Image. Quartz Crystal (Upper) Diamond (Lower) Lens Set at $F-8$. $\times 6$.

Fig. 18 (Right)—Same as Fig. 17 Except that Lens Setting was $F-26$. $\times 6$.

Fig. 19 (Lower)—Showing Effectiveness of Shadows to Indicate Thickness and Degrees of Relief. $\times 6$.

If r is the radius of the aperture of the lens;

$$b = D \frac{2r}{f'}$$

from similar triangles.

Therefore:

$$B = MD \frac{2r}{f^1}$$

We may reduce B by reducing the aperture of the lens but, as noted above, the amount we may do this is limited. For uniform definition in the image the diameter of the focal spot, d, should not exceed b. (Practically, b can usually be considerably greater than d because it is not objectionable, as a rule, to have the more remote portions of the object slightly out of focus if the nearer parts are sharp.) (See Fig. 18.)

Therefore:—

let

$$b = \frac{B}{M} = d = D \frac{2r}{f^1} = 0.0005 F \left(\frac{M+1}{M} \right) \quad \text{See (4)}$$

Then

$$D \frac{2r}{f + D} = 0.0005 F \left(\frac{M+1}{M} \right)$$

since, from Fig. 17, $f^1 = f + D$.

$$\frac{D \cdot 2r}{f + D} = \frac{0.0005 \times 600}{M} = \frac{0.3}{M} \quad \text{See (5)}$$

but

$$f = f_o + \frac{f_o}{M} \quad (\text{Appendix I})$$

Therefore

$$\begin{aligned} D \frac{2r}{f_o + \frac{f_o}{M} + D} &= \frac{0.3}{M} \\ \frac{f_o + \frac{f_o}{M} + D}{2rM D} &= \frac{1}{0.3} \\ \frac{f_o}{2r} + \frac{1}{M} \frac{f_o}{2r} + \frac{D}{f_o} \frac{f_o}{2r} &= \frac{MD}{0.3} \end{aligned}$$

or

$$\frac{f_o}{2r} \left(1 + \frac{1}{M} + \frac{D}{f_o} \right) = \frac{MD}{0.3}$$

But

$$\frac{f_o}{2r} = F = \frac{600}{M+1} \quad \text{See (5)}$$

Therefore

$$\frac{600}{M + 1} \left(1 + \frac{1}{M} + \frac{D}{f_o} \right) = \frac{MD}{0.3}$$

Solving for D;

$$D = \frac{180}{M^2 - \frac{180M}{(M + 1) f_o}} \quad (6)$$

This formula is somewhat cumbersome but, from it we can deduce one important fact. The smaller f_o is, the greater is D. The shorter the rated focal length of the lens, the greater the depth of focus.

Although this may, at first thought, seem paradoxical, the situation becomes clearer when we consider that, for portions of the object which are closest to the lens and which are in sharp focus, no stopping down (i. e. reducing) of the aperture is necessary; and that the effect of stopping down is to make a narrower angle to the pencil of rays subtended by the lens from the more distant parts of the object. Wherefore, the greater the ratio of f^1 to f , the less will the lens have to be stopped down relative to f in order to secure the proper angle relative to f^1 .

This, of course, does not take into account distortion which would become quite objectionable for some types of work if f^1 should be as much as twice f . In general, rectilinear objects of easily recognizable form will stand less distortion, if pleasing results are desired, than curved, indefinitely shaped objects. As a matter of fact, there is no avoiding a certain degree of distortion in this type of picture. To secure normal perspective the objective would have to have a focal length as great as the distance one holds an object away from his eyes for ordinary vision, namely from ten to fifteen inches. This would entail great bellows extensions and give very poor results as regards sharpness of focus. Practically, we are quite accustomed to viewing photographs of all kinds in which the focal length is much less than this and are not usually conscious of the distortion.

Assuming distortion, even to a high degree, to be non-objectionable, one might well ask why an extremely short focal length objective, such as the sixteen or even the four millimeter one, could not be used in place of the longer focus Tessars or Summars, and the answer is, simply, that they have not sufficient covering power. The writer has selected a five by seven plate as the convenient size, and a lens

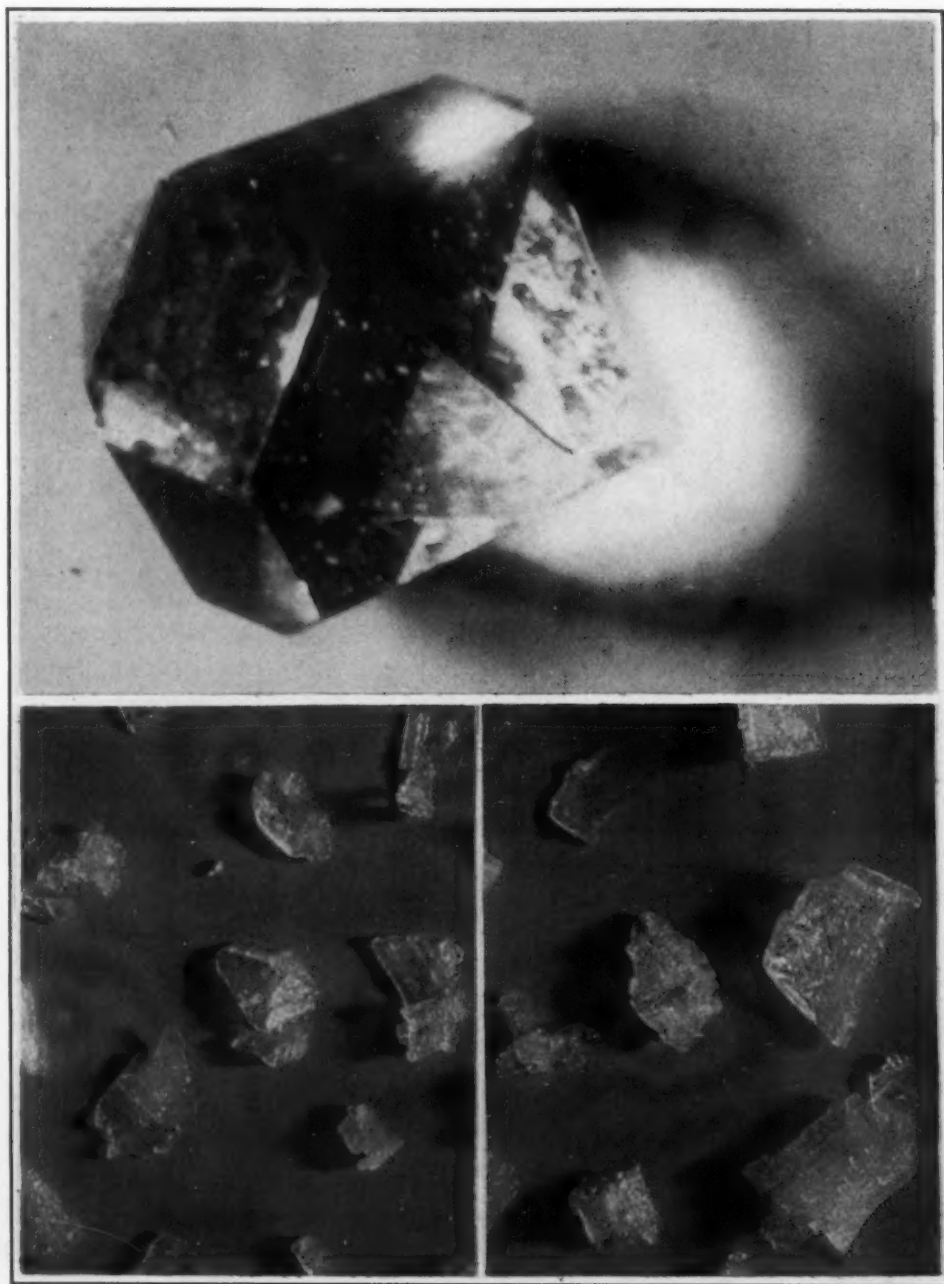


Fig. 20—Quartz Crystal Taken With a Lens Opening of *F*-128. Reduction in Lens Opening Has Been Overstepped.

Fig. 21 (Left)—Thin Salt Crystals. $\times 11$. Fig. 22 (Right)—Thick Salt Crystals. $\times 11$.

must be chosen that will produce an image that covers this plate without being badly out of focus at the corners and without diminution of illumination at the corners. From the above considerations, then, we

would say that the shortest focal length lens that will do this, at the desired magnification, is the one to choose.

Figs. 17 and 18 illustrate the effect of stopping down the aperture to sharpen the image all over. Fig. 20 shows a single quartz crystal where the reduction in aperture has overstepped the limit. Note, however, that the loss in resolution is not quite the same as that of a lens out of focus. In the latter case, lines and dots appear blurred, with hazy indistinct outlines. In the photograph shown, such features have more the appearance of broadened areas with fairly sharp borders. This fact is misleading as regards true resolution of detail, but helps greatly in the attainment of pleasing results.

Wherever possible, three dimensional objects should be so arranged as to give a shadow, not too well defined. Fig. 19 illustrates the effectiveness of this. Shadows also serve to indicate relative thickness and degree of relief, as seen in the salt crystals, Figs. 21 and 22. The author has found the most satisfactory background to be a piece of old, undeveloped photographic plate. This shows no grain at magnifications up to twenty and is usually available.

The above mentioned types of problem seem to the author to be the most important and fundamental in this kind of work. Numerous others arise in the experience of every photomicroscopist and each requires ingenuity and patience. It is no job for the hurry up type of individual who gets the work out "regardless."

APPENDIX

All the considerations contained herein apply, rigorously, only to what are known, optically, as thin lenses. The lenses used in low power work are not, strictly speaking, thin lenses, being composed of several glasses separated by considerable distances. Their behavior is sufficiently close to that of the thin lens, however, so that, within the limits of magnification used, the following derivations and formulæ represent a fair approximation to the facts and are satisfactory for the purpose of the estimations found in the article.

Appendix I

FOCAL LENGTH AND MAGNIFICATION

Let f_0 = the rated focal length of the lens. In the diagram,

the lens is placed edgewise to the paper and the "principal plane" of the lens is a vertical plane, passed through the optical center, and perpendicular to the plane of the paper. It is assumed that the lens has a flat field, and that light, radiating from any point at distance f_o from the principal plane, will emerge on the other side of the lens as rays parallel to the line drawn from that point through the optical center. It is further assumed that f_o is the same on either side of the lens and that it represents not only the distance to the source of rays that emerge parallel, but also the distance to the plane at which parallel rays are brought to a focus by the lens. These considerations are according to elementary optical principles.

Let f = the focal distance from the principal plane to the surface of an object upon which the lens is focussed.

F = the major focal length; that is, the distance from the principal plane to the plane of the magnified image.

M = magnification; that is, a linear dimension in the image divided by the corresponding dimension in the object.

CONSTRUCTION: A line is drawn perpendicular to the principal plane of the lens through its optical center. This is the axis. An object of vertical height O , from the axis, is drawn at

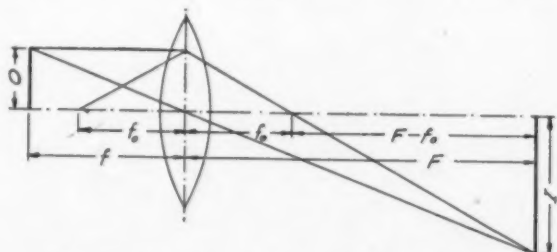


Fig. 23—Diagram Illustrating Focal Length and Magnification.

distance f to the left of the lens. A line representing a ray of light from the upper end of O is drawn parallel to the axis. This is bent downward by the lens to cross the axis at f_o to the right, and continues to the image at I . Another ray, from the upper end of O but through the optical center, crosses the first ray at distance F to the right and thus locates the image.

THEOREM:

$$f = f_o + \frac{f_o}{M}.$$

PROOF:

By similar triangles

$$\frac{I}{O} = \frac{F - f_o}{f_o}$$

and by another pair of triangles

$$\frac{I}{O} = \frac{F}{f}$$

Therefore

$$\frac{F - f_o}{f_o} = \frac{F}{f}$$

$$Ff - f_o f = Ff_o$$

Dividing by $Ff f_o$,

$$\frac{1}{f_o} - \frac{1}{F} = \frac{1}{f}$$

or

$$\frac{1}{F} + \frac{1}{f} = \frac{1}{f_o} \quad (A)$$

This is the well known equation for thin lenses found in texts.

But

$$\frac{I}{O} = M = \frac{F}{f}$$

Therefore

$$F = Mf$$

Substituting in (A)

$$\frac{1}{Mf} + \frac{1}{f} = \frac{1}{f_o}$$

from which

$$\frac{1 + M}{Mf} = \frac{1}{f_o}$$

and

$$f = f_o \left(\frac{M + 1}{M} \right) = f_o \left(1 + \frac{1}{M} \right) = f_o + \frac{f_o}{M}$$

Appendix II

DEPTH OF FOCUS AND DEPTH OF IMAGE

Let f_o = the rated focal length of the lens.

f = the focal length from the principal plane of the lens to the portion of the object nearest the lens.

f^1 = the focal length from the principal plane of the lens to the portion of the object that is farthest from the lens.

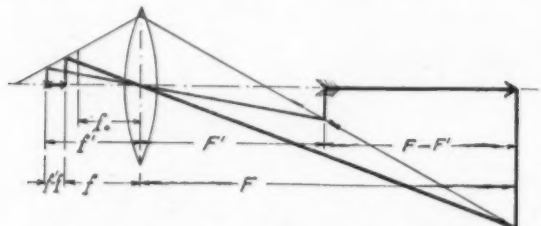


Fig. 24—Diagram Illustrating Depth of Focus and Depth of Image.

F = the major focal length to the ground glass; assuming the lens to be focussed on the portion of the object nearest it, i.e., at f .

F^1 = the major focal length to the image of the portion of the object at f^1 .

M = magnification at F .

M^1 = magnification at F^1 .

$$\text{Since } f = f_0 + \frac{f_0}{M}$$

$$M = \frac{f_0}{f - f_0}; \text{ and similarly, } M^1 = \frac{f_0}{f^1 - f_0},$$

$$F = Mf \quad \text{and} \quad F^1 = M^1 f^1,$$

$$F - F^1 = Mf - M^1 f^1,$$

$$= \frac{f_0 f}{f - f_0} - \frac{f_0 f^1}{f^1 - f_0} = f_0 \left(\frac{f}{f - f_0} - \frac{f^1}{f^1 - f_0} \right)$$

$$= f_0 \left\{ \frac{f (f^1 - f_0) - f^1 (f - f_0)}{(f - f_0) (f^1 - f_0)} \right\}$$

$$= f_0^2 \left\{ \frac{f^1 - f}{(f - f_0) (f^1 - f_0)} \right\}$$

$$= \left(\frac{f_0}{f - f_0} \right) \left(\frac{f_0}{f^1 - f_0} \right) (f^1 - f),$$

$$= M M^1 (f^1 - f).$$

and

$$f^1 - f = \frac{F - F^1}{M M^1}.$$

THE ROLE OF ENERGIZERS IN CARBURIZING COMPOUNDS

BY GEORGE M. ENOS

Abstract

This paper studies the effects of various materials as energizers in carburization and the mechanism of carburization with reference to carbon transfer from the compound to the steel. The experimental work on various phases of carburization are still in progress hence definite conclusion may be premature. However this paper develops the following:

1. Carbonates are not needed as energizers.
2. There are certain materials which will act as catalysts in carburization.
3. There are certain materials which will retard carburization.
4. When only carbon is used as carburizing material a shallow low concentration case is the result.
5. When oxygen of the air is not available, i.e., when the carburizing container is swept with nitrogen, only those energizers which can be readily decomposed to yield oxygen show any effect. It would seem that their sole role is to produce oxygen-carbon compounds or oxygen-iron compounds.
6. Representatives from most of the groups of the periodic system were included in the investigation.
7. Variations in case depth and carbon concentration as produced by different energizers are given.

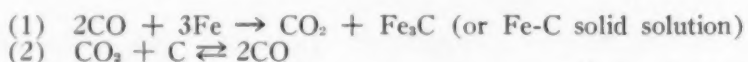
INTRODUCTION

CARBURIZING, an ancient art or process, has been investigated and studied in detail by many workers. A summary of representative views of the mechanism of carburization is included in

This paper is a contribution from the Metallurgical Laboratories, Department of Chemical Engineering, University of Cincinnati. The following have actively cooperated in this investigation: Charles E. Potter, Metallurgist of the McQuay-Norris Manufacturing Co., Connersville, Indiana; and Messrs. Floyd Wile, Arthur Bradley, Herman Swearingen, Carl P. Schneider, seniors in the College of Engineering, University of Cincinnati.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, George M. Enos, is a member of the society and is assistant professor in the Department of Chemical Engineering, University of Cincinnati, Cincinnati, Ohio. Manuscript received June 18, 1931.

the National Metals Handbook, to which reference may be made for details. Herty¹ and his associates have discussed the mechanism of carburizing reactions, but without particular reference to the effect of energizers. The chemical reactions involved are those having to do with the transfer of carbon from the solid carbon of the carburizer to the iron carbide in the case. The formation of the carbide and its diffusion into the steel constitute the essential parts of the carburizing process. The equations usually suggested for the reactions in the "pack hardening" process are:



Since the usual carbonaceous packing materials originally have incorporated in them one or more carbonates of the alkali or alkaline earth metals, it has been customary to consider that



where M is any metal of the alkali or alkaline earth groups.

The CO_2 becomes available for reaction (2) thus tending to produce conditions which will result in a greater concentration of CO and more efficient carburization. Herty states that the CO/CO_2 ratio must be above about 24 for reaction (1) to proceed, and also that the rate of diffusion is on the order of 0.01 to 0.02 millimeters per hour. It may be that the carbonate reacts with the hot carbon:



It is sometimes stated that the energizers, in addition to acting as a source of CO_2 , may function as catalysts for the reaction between the carbon monoxide and the iron, the oxide formed being the catalyst. On standing after a run it has been assumed that the carbonates are regenerated, i. e.,



C. E. Potter and the author² have shown that the energizers do not regenerate to the complete carbonate form, as has been

¹Herty (and associates), "Abnormality in Case-Carburized Steel." Bulletin 45, Mining & Metallurgical Investigations. U. S. Bureau of Mines and Carnegie Institute of Technology, 1929.

²C. E. Potter and G. M. Enos, "Carburization Catalysis," to be published in METAL PROGRESS.

postulated, yet carburization was as efficient on subsequent runs as on the first. Hence it can be definitely stated that the carbonates must be considered merely as the source of the oxides or other compounds formed, by reactions between the carbonates and carbon or by decomposition of the carbonates. These compounds function as catalysts and seem in practice to be effective as long as the physical characteristics of the carburizing compound are not greatly changed, i. e., as long as there are no appreciable dusting losses of the energizer, no contamination of the compound, or disturbances of the physical characteristics.

The purpose of this investigation was to study the effects of various materials as energizers in carburization, and to study the mechanism of carburization with particular reference to the carbon transfer from the "compound" to the iron.

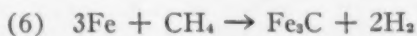
THEORETICAL CONSIDERATIONS

There are several methods which may be suggested, by which carbon may be transferred from the solid form in which it occurs in the carburizing compound to the form of iron carbide in which it is found in the iron which is carburized.

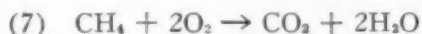
I. First, carbon may simply diffuse or alloy by direct contact, no compounds of oxygen and carbon being formed. The iron at the carburizing temperature is in the gamma condition and theoretically at least can dissolve either the carbon or iron carbide. This method of transfer, if it is effective at all, is of only theoretical interest, since oxygen is available from the air in all commercial practice, and carbon monoxide is certain to form.

II. Second, the carbon monoxide generated by the reaction of solid carbon with oxygen of the air is the carrier for the carbon according to the conventional reactions previously stated (Reactions 1 and 2). Once the reactions are started, it is not necessary to postulate even oxygen of the air, for if the carbon dioxide is reduced to carbon monoxide and no gases escape, the process would be a cyclic one.

III. Third, if any hydrocarbons are present, they may in gaseous form act as carriers of the carbon. A convenient illustration is to assume the presence of methane, when



However, if oxygen be present, it is more likely that



and the CO_2 will be reduced by carbon to form CO.

In pack hardening it is unlikely that reactions of this type are of any importance, although oils, pitch, and other organic materials used as binders in the carburizer might form hydrocarbon gases on heating.

IV. Fourth, it may be that there are side reactions involving the deposition of carbon as such from a gaseous form other than carbon-oxygen compounds, followed by solution of the carbon in the steel. Possibly volatile carbides may be formed. Little is known about these possible side reactions and further speculation is unnecessary here.

No attempt has been made in this work to consider the last two possible methods of carbon transfer. They cannot be utterly dismissed as of no consequence, but the simplifying assumption has been made that the carbon carrier was carbon monoxide, and that the energizers functioned in the manner suggested in the paper by Potter and Enos.³ It will be shown later that there is little probability of direct carbon transfer by contact diffusion and on this basis Case I is of little practical importance. The conditions in pack hardening are these:

The low carbon steel (or other ferrous material) is raised to a temperature such that austenite can exist. When a source of carbon, such as carbon monoxide, is brought into contact with the hot steel, cementation occurs. It is usually desired to have the cementation proceed to certain depths with a carbon concentration in the neighborhood of the eutectoid. For any given depth a certain time is required for any definite temperature used, assuming a con-

³It has been suggested by Prof. R. S. Tour that the role of the energizers is that of acting as intermediate compounds in the carbon transfer, according to the reactions:

1. $9\text{FeO} + 3\text{CO} \rightleftharpoons 3\text{Fe}_3\text{O}_4 + 3\text{C}$
The carbon is in active form and available for equation 4.
- Step I 2. $3\text{Fe}_3\text{O}_4 + 3\text{CO} = 9\text{FeO} + 3\text{CO}_2$
3. $3\text{CO}_2 + 3\text{C (carbon base)} \rightleftharpoons 6\text{CO}$
The CO formed is available for Equations 1 and 2.
4. $2\text{BaO} + 6\text{C (active carbon)} \rightleftharpoons 2\text{BaC}_2 + 2\text{CO}$
The CO formed is available for Equation 6.
- Step II 5. $2\text{BaC}_2 + 9\text{Fe} \rightleftharpoons \text{Ba}_2\text{C} + 3\text{Fe}_3\text{C}$
 Fe_3C is absorbed in the steel.
6. $\text{Ba}_2\text{C} + 2\text{CO} \rightleftharpoons 2\text{BaO} + 3\text{C (active carbon)}$
The active carbon and BaO are available for Equation 4.

In the case of energizers other than barium compounds equivalent sets of reactions might be written. It is not known positively that the carbides of barium are formed, but the set of equations serves as an illustration of the intermediate compound theory of catalysis.

stant supply and concentration of carbon monoxide. If too much carbon is concentrated in the outer layers of the steel, that is, if absorption, or solution, or reaction is proceeding faster than diffusion, the final case is undesirable because it will be too high in carbon and require too much subsequent heat treatment to diffuse the carbon. If, on the other hand, an inadequate supply of carbon is available, that is, the reactions, or absorption, or solution of carbon are proceeding at less than the diffusion rate, the depth of case may be great, but the carbon concentration relatively low. The ideal conditions are, (1) to use a temperature such that grain growth is not excessive, (2) to pass carbon into the steel at such a rate that diffusion will occur at a rate which will just permit the desired percentage of carbon to be present in the case at all times.

If the carburizer be considered for the moment as a simple form of carbon, with an energizer present, for example, wood charcoal, with its ash content functioning as the energizer, then it is conceivable that the addition of other materials might accelerate the carburizing reactions or might retard them. Mahin and Mootz⁴ have shown that the efficiency of ferrosilicon as an addition agent in carburization depends on the fineness of the ferrosilicon. The addition of ferrosilicon regulates the rate at which carburization proceeds so that a hypereutectoid case is not formed, where without it the hypereutectoid case would be formed with the carburizing compound and temperature they used.

We may then regard ferrosilicon as a negative catalyst when added to a commercial carburizing compound. It may function as an "intermediate" compound, or function because of surface effects, or by virtue of both effects.

Having shown that carbonates as such are not necessary in carburization, and that a material like ferrosilicon functions as a catalyst, it is logical to look for other materials which might accelerate or retard the carburization rate. The variables of volume, temperature, and hence pressure, can be maintained constant within experimental limits. Other variables can be controlled and a study made of the effects of specific materials as energizers.

EXPERIMENTAL PROCEDURE

Representative oxides from the various groups of the periodic

⁴Mahin and Mootz, "The Modifying Action of Ferrosilicon on the Carburization Process," *TRANSACTIONS, American Society for Steel Treating*, Vol. 18, 1930, p. 552.

system were selected for trial, as well as a group of miscellaneous materials, such as carbides, natural minerals of the silicate type, and some others. The carbon base materials were wood charcoal and pure sugar carbon. For comparison, a commercial carburizer (Compound B, Table I) and a home made standard mix carburizer were included in each run where the special energizers were used.

Preparation of "Special" Compounds

Wood charcoal was obtained from a commercial source and was crushed and screened. The charcoal used throughout the investigation was from one lot. The material used as a carbon base would pass an 8-mesh standard screen and rest on 35-mesh screen. The charcoal contained less than 2 per cent moisture and had an ash content of 3.1 per cent. The materials used as energizers were crushed to pass 8-mesh and rest on 35-mesh in most cases, although for some special reagents it was not practical to obtain material this coarse. It is not believed that errors introduced in this way are appreciable, as some experimental runs with variations in particle size of the energizer with some common reagents did not produce appreciable differences in case depth or carbon concentration unless the particles were too coarse to mix intimately with the carbon base.

Various methods of binding were considered, but since the "compound" was to be used but once, no special means of binding was employed. The charcoal, about 30 grams for each charge, was weighed out on a clean paper, and 15 per cent by weight of the energizer incorporated by rolling thoroughly. Each charge was weighed separately and placed in its container without further handling.

Containers and Packing

Each sample was packed in an individual container. The containers used were quarter pint tin cans fitted with friction lids. Neither the compound nor the container were used a second time. The packing was carried out as follows—The steel sample was placed on a bed of the carburizer, about one-third of the total charge, and then covered with the balance of the charge. A piece of pure Swedish iron wire of sufficient size to furnish samples for carbon determinations, if desired, was coiled loosely about each sample and buried in the compound.

Steel Samples

Some preliminary runs were made on one half-inch rounds of S.A.E. 1020 steel. Unless otherwise noted in the tabulated data, the samples used were hollow cylinders 0.75 inches outside diameter and 0.433 inches inside diameter, cut to a length of 1.25 inches. They were ground on a centerless grinder, notched to facilitate breaking, numbered and cleaned. The cleaning was carried out as follows: The samples were immersed in a hot alkaline cleaner for about 5 minutes to remove traces of oil, then immersed in hot dilute sulphuric acid for one minute, then dipped in clean boiling water, dried and stored in desiccators. The analysis of the steel was as follows: Carbon 0.22 per cent, Silicon 0.11 per cent, Manganese 0.36 per cent, Sulphur 0.035 per cent, Phosphorus 0.021 per cent. The steel was one known to produce a normal case.

Carburization

The containers were placed in lots of 30 to 40 in a gas-fired furnace equipped so that the temperature and furnace atmosphere could be closely controlled. The furnace was brought up to heat in not less than two hours and held at 1680 degrees Fahr. for six hours. The furnace was cooled slowly to permit complete cementite precipitation.

Preparation and Study of Carburized Samples

The samples were removed from the containers, fractured, and qualitative notes made of the fractures. They were then sectioned with a hack saw so that the cross-section after polishing and etching would show the true depth of case. By this method it was possible to obtain four representative samples for microscopic examination from each carburized sample. However, it was customary to polish and examine but one sample section from each run except where check measurements were made on case depth in another laboratory. Before polishing, the samples were cleaned by immersing in hot alkali cleaner, followed by immersion successively in hot water, hot dilute sulphuric acid (1 minute), and hot water.

Case measurements were made on the inside and outside of the polished and etched samples by projecting the structure at 100 diameters magnification on the ground glass screen of the metal-

Table I
Characteristics of Carbon Bases and Common Carburizing Compounds. Time, 6 Hours at Heat. Temp. 1680 Degrees Fahr.

Material	No. of Runs	Maximum Carbon Per Cent Estimated	Case Depth, in Inches		Case Depth Variation, in Inches	
			Average		Max.	Min.
Charcoal	6	0.65	0.028		0.039	0.020
Sugar Carbon	6	0.3	trace	
Compound B ¹	6	Hypereutectoid	² Complete	Hyper-eutectoid	0.025
Standard ³	6	Hypereutectoid	Complete		0.015
					Complete	0.016

¹Compound B. A pitch coke base, Energizer proportions, 15 per cent BaCO₃, 3 per cent CaCO₃, 2 per cent Na₂CO₃.

²Complete indicates carbon penetration to one half the thickness of sample.

³"Standard," a home made compound, using the standard wood charcoal, and incorporating mechanically 15 per cent BaCO₃, 1.5 per cent CaCO₃ and not over 2 per cent Na₂CO₃.

lographic camera. Measurements were checked on each sample by an independent observer.

The carbon concentrations were qualitatively noted from the microstructure. Some analyses were made for carbon content in the iron wires which were also carburized. These analyses showed appreciably higher carbon concentration, as was expected.

Summarized data from the investigation is given in Tables I, II, III, and IV. The temperature was held as near 1680 degrees Fahr. as possible, the maximum deviation usually being of the order of ± 10 degrees Fahr. Time period at heat was six hours.

DISCUSSION OF RESULTS

In Table I is given the average values for the carburizing materials which were included in each run for purposes of comparison. Steel samples in duplicate were run with each carburizing mix, but as stated before, the samples were in individual containers. As will be noted from the various tables, more than two samples were run with certain mixes, but not more than two were included in any one heat.

Referring to the carburizing mixes included for comparison, it will be seen that the sugar carbon gave consistent results in that only a slight increase of carbon concentration could be observed in the shallow case obtained (see Fig. 2-b). Compound B gave very consistent results throughout all the runs. A representative photomicrograph is shown in Fig. 2-c. Charcoal gave cases of various

Table II

Characteristics of Carbonate Energized Compounds (15 Per Cent by Weight of Energizer).
Time, 6 Hours at Heat. Temp. 1680 Degrees Fahr.

Material	No. of Runs	Maximum Carbon Per Cent Estimated	Case Depth in Inches, Average	Case Depth Variations in Inches,	
				Max.	Min.
Sodium Carbonate	4	Hypereutectoid	0.036	0.047	0.024
Potassium Carbonate	3	Hypereutectoid	0.035	0.048	0.020
Magnesium Carbonate	2	0.6	0.042	0.045	0.040
Calcium Carbonate	2	0.4	0.036	0.040	0.035
Strontium Carbonate	2	0.8	0.047	0.060	0.035
Barium Carbonate	5	Hypereutectoid	0.040	0.059	0.028

Table III

Characteristics of Oxide Energized Compounds (15 Per Cent by Weight of Energizer).
Time, 6 Hours at Heat. Temp. 1680 Degrees Fahr.

Material	No. of Runs	Maximum Carbon Per Cent Estimated	Case Depth in Inches, Average	Case Depth Variations in Inches,	
				Max.	Min.
Magnesium oxide, MgO	4	0.85	0.047	0.050	0.040
Barium oxide, BaO	2	0.9	0.035	0.040	0.031
Boron oxide, B ₂ O ₃	2	0.6	0.035	0.040	0.030
Aluminum oxide, Al ₂ O ₃	4	0.4	0.038	0.045	0.030
*Silicon dioxide, SiO ₂	6	0.4	0.025	0.035	0.015
Titanium oxide, TiO ₂	7	0.7	0.051	Complete	0.015
Zirconium oxide, ZrO ₂	2	0.4	0.033	0.035	0.030
Cerium oxide, CeO ₂	4	0.8	0.027	0.039	0.015
Chromium oxide, CrO ₂	2	0.3	0.015	0.020	0.015
Manganese oxide, MnO ₂	2	0.3	0.028	0.035	0.024
Iron oxide, Fe ₂ O ₃	4	0.4	0.030	0.035	0.025

*Various types of silica were used. The value here given is an average value. See Table VII.

Table IV

Characteristics of Some Miscellaneous Materials Used as Energizers With Wood Charcoal. 15 Per Cent by Weight of Energizer. Time, 6 Hours at Heat.
Temp. 1680 Degrees Fahr.

Material	No. of Runs	Maximum Carbon Per Cent Estimated	Case Depth in Inches, Average	Case Depth Variations in Inches,	
				Max.	Min.
Borax Glass, Na ₂ B ₄ O ₇	2	0.4	0.020	0.030	0.010
Feldspar, K ₂ O.Al ₂ O ₃ .6SiO ₂	2	0.4	0.042	0.047	0.040
Silicon	2	0.4	0.040	0.045	0.030
Ferrosilicon (50-50)	2	0.85	0.040	0.040	0.035
Silicon carbide	2	0.4	0.040	0.050	0.035
Ferrovanadium	2	0.7	0.040	0.045	0.035
Calcium carbide	2	0.4	0.031	0.035	0.030

depths, but the carbon concentration was quite consistent, that is, it was usually about 0.6 or 0.7 per cent as a maximum (see Fig. 2-a).

The results from the home made carburizing compound were

consistent for the earlier runs. On later runs considerable variation was observed, due probably to segregation or loss of energizers during storage and handling.

Table II gives the results obtained with various carbonates of the alkali and alkali earth metals. The variations in case depth for par-

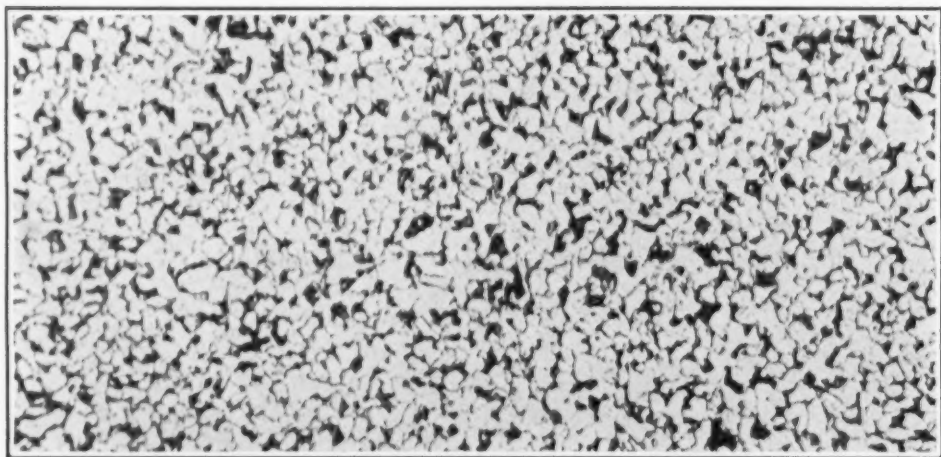


Fig. 1—Microstructure of the Steel Used in This Investigation. As Received. Etched in Nital. $\times 100$.

ticular mix may be due to the charcoal variations. The maximum carbon concentration on the duplicate samples was reasonably constant.

In considering the oxides listed in Table III it will be noticed that appreciable case depths were obtained with some of those listed. No hypereutectoid cases were produced, but magnesium oxide, barium oxide, cerium oxide and titanium oxide produced cases of sufficient carbon concentration and great enough depth to indicate conclusively that they did act as energizers. Magnesium oxide actually produced a deeper case with greater concentration than magnesium carbonate. Barium oxide did not produce quite as deep a case or quite as great a carbon concentration as the carbonate. The data in the Tables II and III are indicative of the effects of the various materials when used as energizers. However, the oxides represent a greater concentration than the carbonates, since the compounds left by the breakdown of the carbonates would be less in actual weight than the oxides added as such, if we assume that only oxides are formed. If complex compounds are formed, no definite statement can be made as to relative weight percentage.

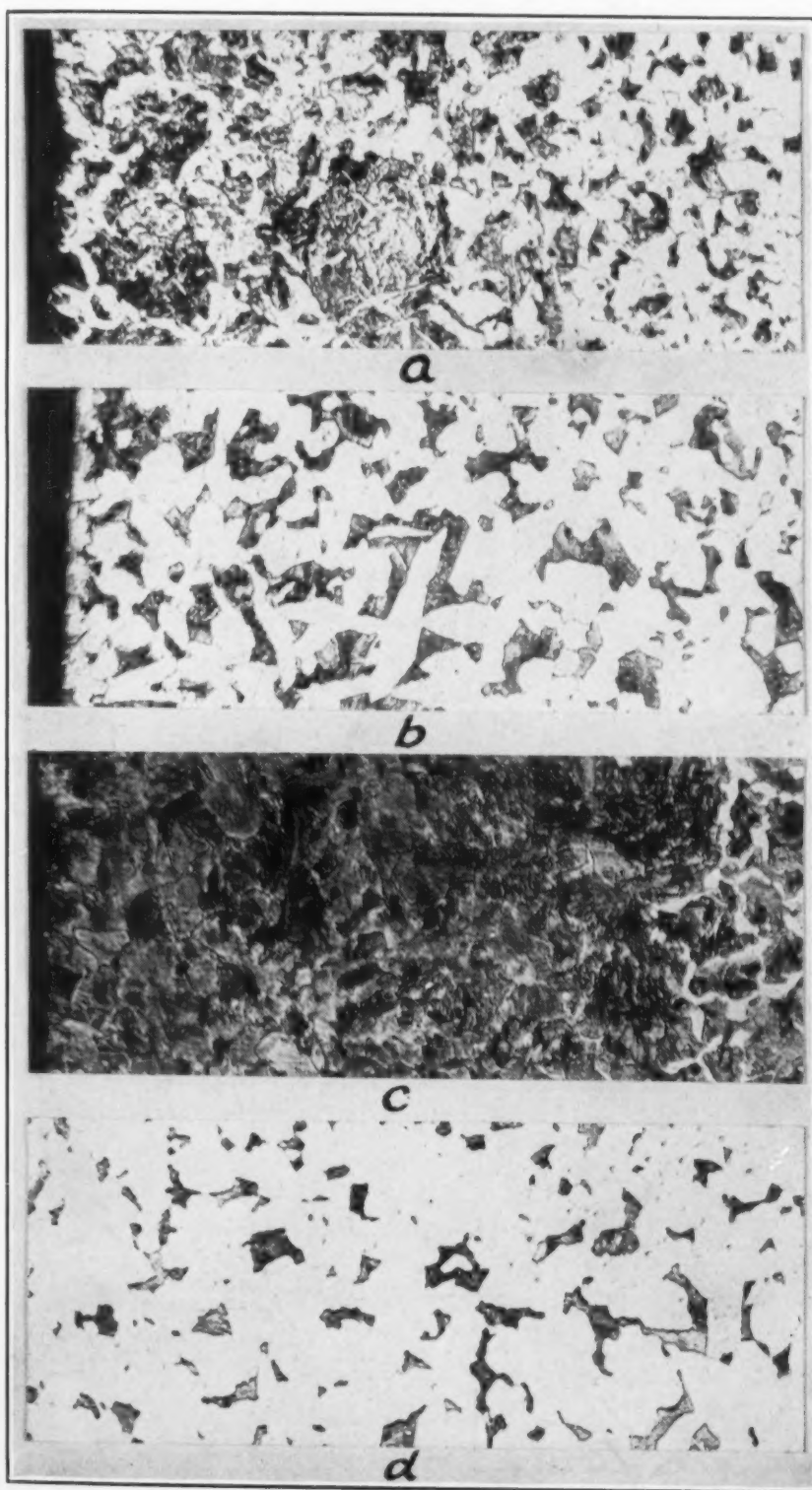


Fig. 2—(a) Structure of Case Produced by Charcoal Alone. (b) Structure of Case Produced by Sugar Carbon. (c) Structure of Case Produced by Compound B. (d) Typical Core Structure, No Increase in Carbon Content. Etched in Nital. All Photomicrographs $\times 100$.

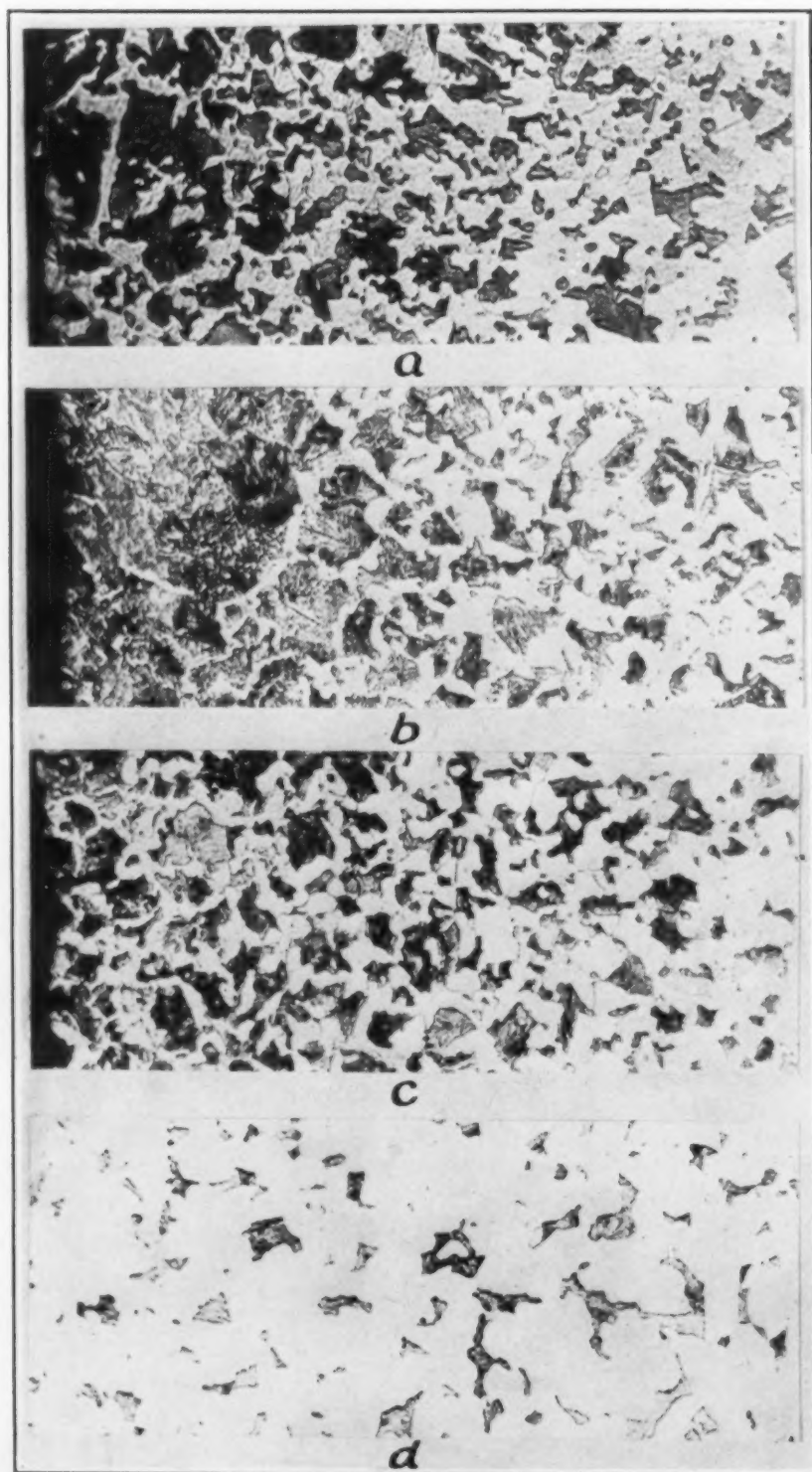


Fig. 3—(a) Structure of Case Produced with Barium Carbonate as the Energizer. (b) Structure of Case Produced with Barium Oxide as the Energizer. (c) Structure of Case Produced with Magnesium Oxide as the Energizer. (d) Typical Core Structure, No Increase in Carbon Content. Etched in Nital. All Photomicrographs $\times 100$.

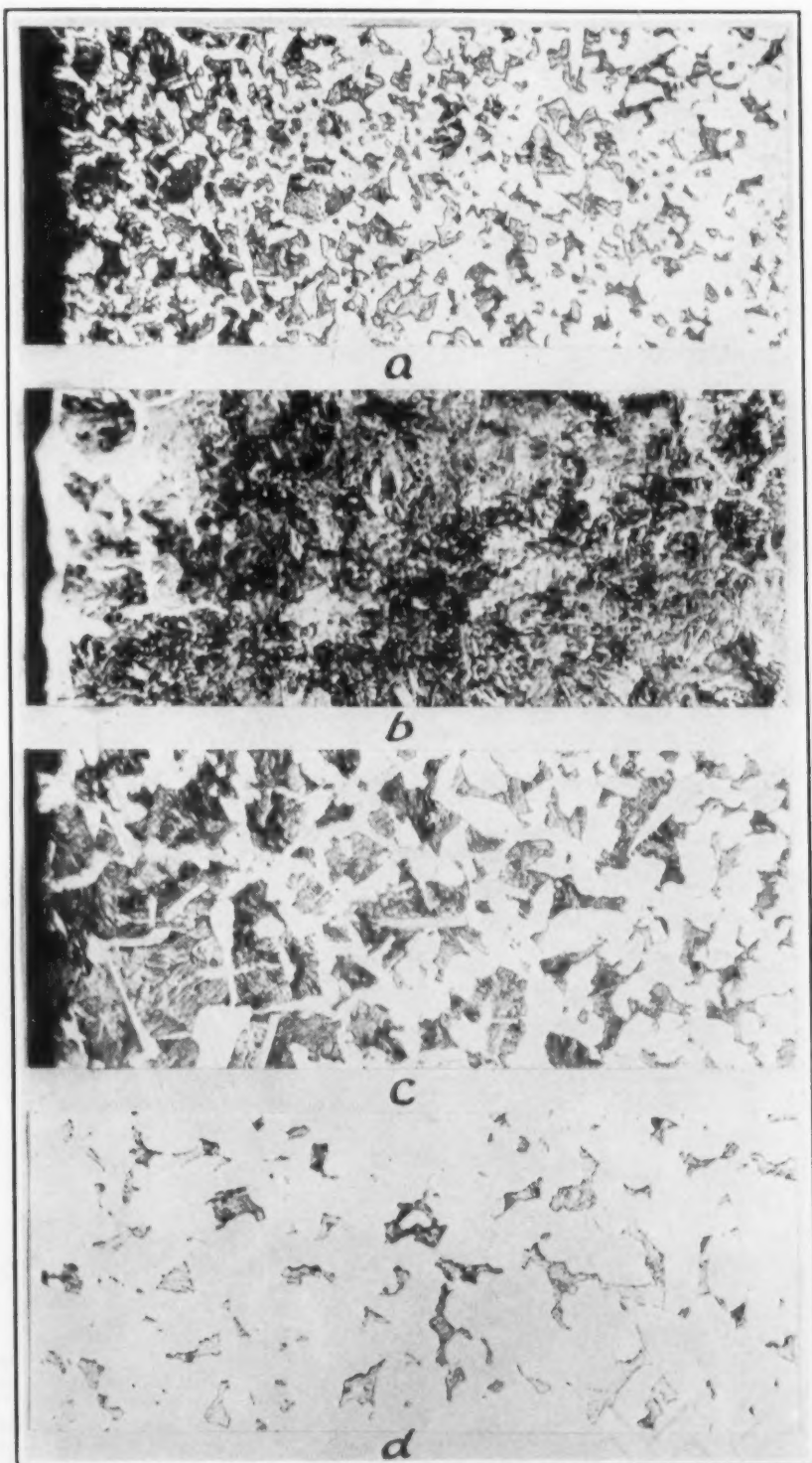


Fig. 4—(a) Structure of Case Produced with Calcium Carbonate as the Energizer. (b) Structure of Case Produced with Potassium Carbonate as the Energizer. (c) Structure of Case Produced with Ferrosilicon as the Energizer. (d) Typical Core Structure, No Increase in Carbon Content. Etched in Nital. All Photomicrographs $\times 100$.

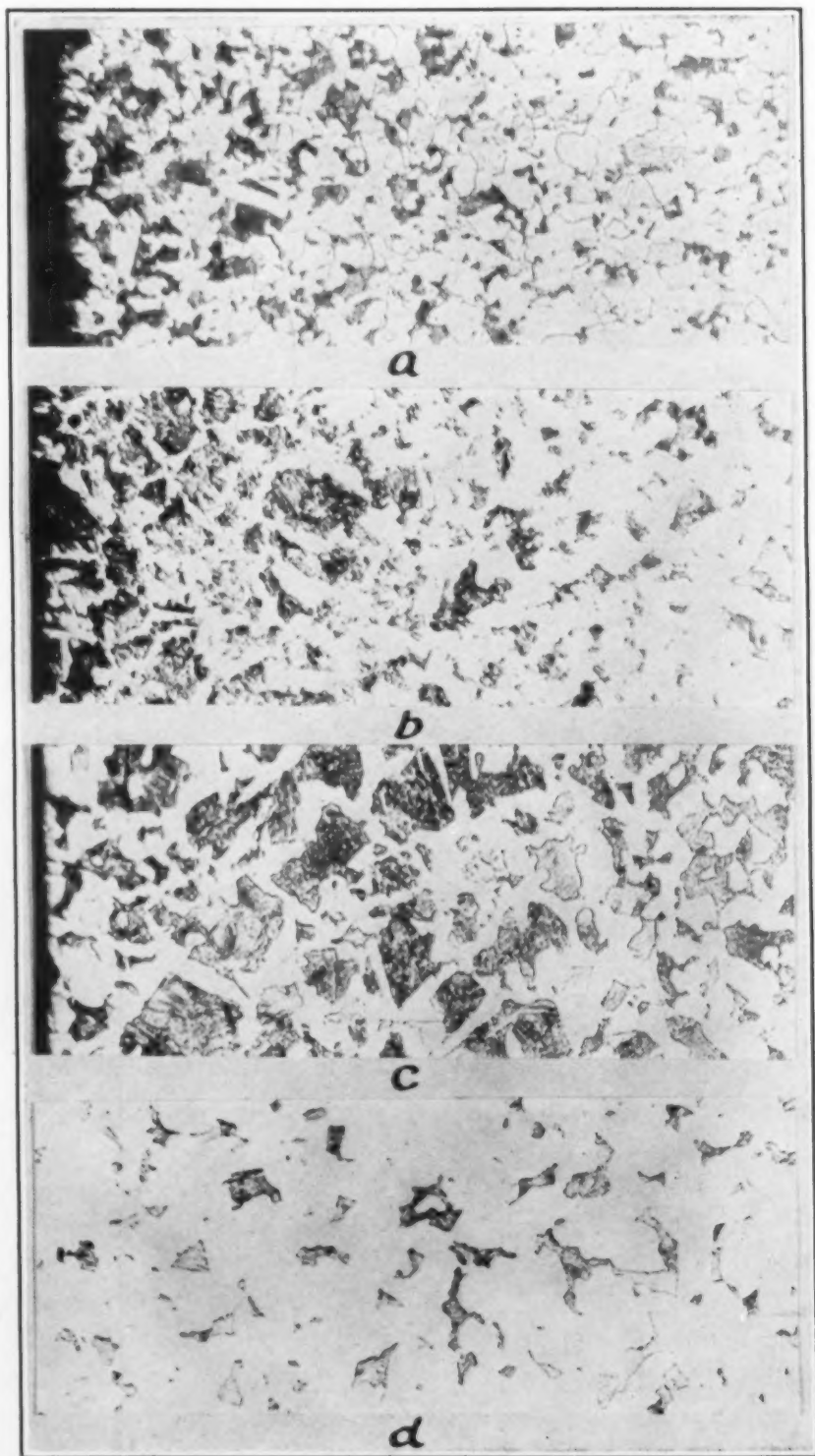


Fig. 5—(a) Structure of Case Produced with Ferric Oxide as the Energizer. (b) Structure of Case Produced with Aluminum Oxide as the Energizer. (c) Structure of Case Produced with Titanium Oxide as the Energizer. (d) Typical Core Structure, No Increase in Carbon Content, Etched in Nital. All Photomicrographs $\times 100$.

Aluminum oxide, silica, zirconium oxide, chromium oxide, manganese oxide, and iron oxide produced cases of less carbon concentration than wood charcoal, but only one, chromium oxide, gave appreciably less depth of case. Boron oxide probably exerted little or no effect on the charcoal. The miscellaneous materials listed in Table IV produced greater case depths than those produced by charcoal alone, with one exception, borax glass. However, the carbon concentration was less than that produced by charcoal in all cases except where ferrosilicon or ferrovanadium were used as energizers.

While a direct comparison with the work of Mahin and his associates cannot be made because of different procedures in the experimental work, it is interesting to note that a case of high carbon concentration, approaching the eutectoid at the edge, was obtained using ferrosilicon as the only addition to the charcoal.

In a previous investigation Chas. E. Potter and the author had suggested a mechanism of carburization, based on the formation of carbides of alkaline earth or alkali metals as "intermediate" compounds. For this reason two carbides were included in the runs, calcium carbide as a representative alkaline earth metal carbide, and silicon carbide as a representative of a dissimilar type of carbides. In neither case did the carbon concentration reach that produced by wood charcoal alone, although the case depth was greater in both cases. It may be that these two carbides are not as efficient as catalysts as is barium carbide and hence the theory cannot be rejected on the basis of these runs.

The other materials listed in this table were included for the following reasons:—silicon because of its relation to ferrosilicon, borax glass and feldspar to see the effects obtained when light metals were chemically combined in relatively complex stable compounds.

All of the samples were examined in detail at 100 diameters magnification, and many were examined at higher magnifications. All average case depth measurements were the average of the inside case, and the outside case measurements as well as the average of several samples. Representative samples were photographed and the photomicrographs are shown in Figs. 2 to 5. In each plate a typical core structure is included for comparison. This structure is that of the original steel held for 6 hours at 1680 degrees Fahr. and cooled with the furnace. The structure of the steel as received is shown in Fig. 1.

As a result of the experimental work reported so far it seems

evident that many materials other than carbonates may act as energizers in increasing case depth, and carbon concentration, over that obtainable with the charcoal base alone.

A few runs were made with sugar carbon as the base. The procedure employed was the same as previously described. When sodium carbonate was used as the energizer, 15 per cent by weight, apparently complete carburization had been attained, as the core showed about 0.6 per cent carbon concentration. The outer edges were completely decarburized to a depth of 0.020-0.030 inches. Ferrosilicon did not produce any marked increase in carbon, but decarburization was so deep that it may have been carburized at one time to a slight depth. Silica gel produced similar results. Some further runs were made using $\frac{1}{2}$ inch diameter rods of approximately the same carbon content as the hollow cylinders used regularly. These results are given in Table VI. In this work, while decarburization did occur, it was possible to determine that a shallow case of low carbon content had actually been formed when silica was the only material added to pure sugar carbon. The difference between cases produced by sugar carbon alone, as compared to silica-energized sugar carbon, are not great, but can be noticed by a careful observer when the cases are compared under a microscope.

It is not known positively at this time whether or not the energizing effect of the various materials would be maintained on successive runs, but if the materials were incorporated properly with the carbon base there is every reason to believe that the compounds would stand up in service.

It is often desirable in practice not to have a hypereutectoid case, but to have one of eutectoid composition or with even less carbon, with an appreciable depth. It would seem possible to obtain any desired carbon concentration with a reasonable depth of case merely by varying the type of energizer. Although the percentages which might be used have not been investigated in all cases, if 15 per cent energizer is used it is possible to group the energizers according to the carbon concentration produced. This has been done in Table V for a representative group. It will be observed that the case depth of each material listed is greater than that of the wood charcoal used as the base.

It is possible to reduce the carbon concentration, as with feldspar and calcium carbonate, maintain it about the same as the wood charcoal, with titanium oxide and magnesium oxide, or to increase to the

Table V
Selected List. Energizers Grouped According to Carbon Concentration Produced with
a 15 Per Cent Addition to Charcoal Base. Time at Heat, 6 Hours.
Temperature 1680 Degrees Fahr.

Materials	Maximum Carbon Per Cent	Average Case Depth, in Inches
Feldspar	0.4-0.5	0.042
CaCO ₃	0.4-0.5	0.036
Boron oxide	0.6-0.7	0.035
Wood charcoal	0.6-0.7	0.028
Titanium oxide	0.6-0.7	0.038
Magnesium oxide	0.8-0.9	0.047
Barium oxide	0.8-0.9	0.037
Ferrosilicon (50-50)	0.8-0.9	0.040
Barium carbonate	Hypereutectoid	0.040

eutectoid with magnesium oxide, barium oxide or ferrosilicon. The energizers used to produce a hypereutectoid case were carbonates of sodium, potassium or barium either singly or in combination with other energizers.

While most of the work reported here was done with a 15 per cent addition of the energizer to the charcoal, two materials were selected for study as to variation in proportion of the energizer. Silica was selected as an example of what may be termed a "negative energizer" when used with a charcoal base with 15 per cent addition, while titanium was selected because a rather deep case was produced, on the average, over that obtainable with wood charcoal, without increasing the carbon concentration.

The data for variations of silica content, type of silica used, and type of carbon base used are included in Table VI. It will be noted that in no case, with any variation in source or percentage of silica added, is there any marked increase in carbon concentration or in case depth over that obtainable with the carbon base when used alone. When the silica is added to a commercial carburizing compound it greatly reduces the carbon concentration and case depth. Part of this effect might be caused by dilution, but certainly not all of it can be traced to that cause. Silica, with charcoal or a commercial carburizing compound, can be regarded in general as a negative catalyst or energizer. With sugar carbon its qualitative effect, although slight, seems to be as a positive catalyst.

In Table VII the data for some variations in percentage of titanium oxide are given. In general, the case depth is not effected by change in percentage of titanium oxide added. With an addition of 15 per cent the average value is high, but as was noted in Table

Table VI
Data on Variations in Percentage and Source of Silica Added as an Energizer to
Different Carbon Bases. Time, 6 Hours at Heat. Temperature 1680 Degrees Fahr.

Carbon Base	Per Cent SiO ₂	Source of SiO ₂	Depth of Case in Inches, Average	Max. Per Cent Carbon Estimated	Steel
Sugar carbon	5	white sand	trace	0.3	½ inch diam. solid cylinders S.A.E. 1020
Sugar carbon	15	white sand	0.010	0.3	
Sugar carbon	25	white sand	0.020	0.3	
Sugar carbon	25	white sand	trace	0.3	
Sugar carbon	50	white sand	0.024	0.3	
Sugar carbon	trace	0.3	
Wood Charcoal	1	white sand	trace	0.3	
Wood Charcoal	5	white sand	trace	0.3	
Wood Charcoal	10	white sand	trace	0.3	Usual ¾ inch O.D. hollow cylinders S.A.E. 1020
Wood Charcoal	15	white sand	trace	0.3	
Wood Charcoal	15	c.p. SiO ₂	0.020	0.3	
Wood Charcoal	15	c.p. SiO ₂	0.020	0.3	
Wood Charcoal	15	silica gel	0.030	0.3-0.4	
Wood Charcoal	15	silica gel	0.030	0.3-0.4	
Wood Charcoal	15	alundum	0.035	0.4	
Wood Charcoal	15	alundum	0.035	0.4	
Wood Charcoal	15	quartz	trace	0.4	½ inch diam. solid cylinders S.A.E. 1020
Wood Charcoal	15	quartz	trace	0.4	
Wood Charcoal	0.028	0.65	
Compound B	10	white sand	0.040	0.5	
Compound B	20	white sand	0.035	0.7	
Compound B	20	white sand	0.024	0.6	
Compound B	50	white sand	0.032	0.7	
Compound B	Complete	Hypereutectoid	

Table VII
Data on Variations in Percentage of Titanium Oxide (Rutile) Used as an Energizer,
Wood Charcoal Base. Time, 6 Hours at Heat, Temperature 1680 Degrees Fahr.

Per Cent Titanium Oxide (Charcoal only)	Average Depth of Case in Inches	No. of Runs	Max. Per Cent Carbon Estimated
1 per cent	0.030	2	0.7
3	0.025	2	0.7
5	0.036	2	0.5
10	0.036	2	0.6
15	0.033	2	0.7
	0.051	7	0.7
5% TiO ₂ + 1.5% Na ₂ CO ₃	0.022	2	0.5
10% TiO ₂ + 1.5% Na ₂ CO ₃	0.024	2	0.7
15% TiO ₂ + 1.5% Na ₂ CO ₃	0.027	2	0.6
5% TiO ₂ + 5% Na ₂ CO ₃	0.040	1	0.8

III the variations in case depth between samples are great. No appreciable change in carbon concentration could be noted with different percentages of titanium oxide addition. In an attempt to increase the carbon concentration and maintain the desired depth, various percentages of sodium carbonate were added as promoters. One combination, 5 per cent of each, was found which was satis-

factory, but this result was not checked. The other values listed cannot be regarded as satisfactory.

THE MECHANISM OF CARBON TRANSFER

Some attempts were made to investigate whether or not samples must be packed in a solid compound, or whether the "gases" generated will be effective at some distance. There is no question but that carbon-bearing gases such as carbon monoxide or various hydrocarbons are efficient cements when fed to a carburizing container under controlled conditions. The point at issue was whether the gases generated from a solid carburizing compound would be effective at short distances from the compound itself. The steel samples were prepared in the usual way, and suspended from the lids of the carburizing cans, at a height of about $\frac{1}{2}$ inch above the carburizing compound, one sample to a can. Five "compounds" were used, viz., sugar carbon, sugar carbon plus 15 per cent sodium carbonate, sugar carbon plus 15 per cent ferrosilicon, sugar carbon plus 15 per cent silica gel, compound B.

The qualitative results were as follows: The samples suspended above the ferrosilicon and silica gel-energized mixes were completely decarburized. The sample above the sodium carbonate mix was free from carbon in the core, but a very slight carbon concentration was still evident in the outer surfaces. The sample above the commercial compound was carburized slightly on the surface nearest the compound. It is suggested that a decarburizing atmosphere predominated in the cans where no carbonate was present, and was less decarburizing in the cans where carbonate was present. This matter is being investigated further.

The next line of attack was to attempt carburization under conditions where little or no oxygen of the air would be available. While carburizing in such a manner that a vacuum could be imposed might have some advantages, it was decided to use a system where nitrogen would be the only gas present aside from such amounts of carbon-bearing gases as might be formed from the carburizer in the absence of oxygen of the air.

The apparatus used is shown in Fig. 6. A one-inch nickel tube (A) was fitted with a thermocouple, and placed in an electric tube furnace. Nitrogen was supplied from the cylinder at (D) and passed through two wash bottles of alkalin pyrogallol at (C), then through

a heated tube containing copper turnings (F). This set-up should remove any oxygen in the nitrogen. The nitrogen then passed through two wash bottles of concentrated sulphuric acid (B), thus removing moisture, then through the nickel tube, escaping through a beaker of sulphuric acid (E) which served as a valve to prevent air from entering the apparatus in case of diminution of the volume of

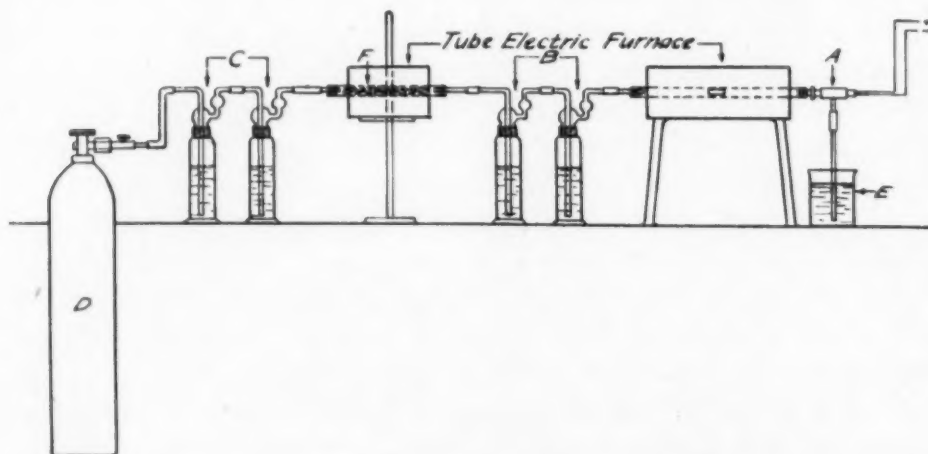


Fig. 6—Diagram of Apparatus Used in Carburizing in an Atmosphere of Nitrogen. A, Nickel Tube; B, Wash Bottles of Concentrated Sulphuric Acid; C, Wash Bottles of Alkaline Pyrogallol; D, Cylinder of Nitrogen; E, Beaker of Concentrated Sulphuric Acid; F, Tube Containing Copper Turnings.

gas due to any cause. In this way a positive pressure of nitrogen could be maintained, thus excluding air from entering the tube.

In the experiments hollow cylinders, previously described, were fitted with various carburizing mixtures, and the ends plugged lightly with steel wool so that the nitrogen was free to circulate through the carburizing compound. The tube was swept with nitrogen from the time the furnace was started at room temperature, until it was again cool. The samples were heated one at a time, to 1680 degrees Fahr. and held at that temperature for 6 hours. The heating period and cooling periods were each about one and one half hours long. After cooling, the samples were fractured, polished, etched and case depths measured in the same manner as previously described. Of course only the inside edge of the sample would be available for carburizing when the carburizing compound was packed inside the tube. Other samples, with other conditions, were also run in the same furnace.

The results are given in Table VIII. Runs No. 1 and 2, where carbonates were present, showed a small increase in carbon concentration to an appreciable depth. The barium oxide used in Run 3

Table VIII
Data on Carburization in an Atmosphere of Nitrogen. Time, 6 Hours at Heat,
Temperature 1680 Degrees Fahr.

Run No.	Material	Case Depth in Inches	Max. Per Cent Carbon Estimated
1	Compound B	0.030	0.30
2	Wood charcoal + 15% BaCO ₃	0.030	0.40
3	Wood charcoal + 15% BaO	0.40	0.80
4	Wood charcoal + 15% BaO	0.0	0.20
5	Wood charcoal + 15% TiO ₂	0.0	0.20
6	Wood charcoal + 15% Feldspar	0.0	0.20
7	Wood charcoal	0.0	0.20
8	Wood charcoal + 15% ferrosilicon	0.0	0.20
9	Wood charcoal + 15% MgO	0.0	0.20
10	Compound B ¹	0.0	0.20
11	Compound B ²	0.0	0.20
12	Compound B ³	0.0	Decarburized
13	Compound B ⁴	0.08	0.50

¹Carburizer in path of nitrogen stream ahead of sample but not in intimate contact.

²Carburizer adjacent to sample, no nitrogen flowing, tube open.

³Carburizer packed loosely around sample, no nitrogen flowing, tube open.

⁴Carburizer packed inside of tube, tube open, no nitrogen flowing.

was formed by heating barium peroxide to a temperature of 900 degrees Cent. (1650 degrees Fahr.), but it is probable that it formed the peroxide completely, or in part, on cooling. The barium oxide used in Run 4 was formed from barium nitrate and was probably completely BaO. The other materials used, Runs 5 to 9 inclusive, were some of those which previous experience had shown would produce good cases under pack hardening conditions. Compound B was run under various conditions as noted.

When carburizing in the absence of oxygen it seems evident that carburization is not accomplished, at least under the conditions present in this investigation. The energizers do not function under these conditions unless they can be decomposed to liberate oxygen, that is, form iron-oxygen or carbon-oxygen compounds. While not conclusive and final evidence, the work here indicates that the role of the energizers as catalysts is confined to their effect on the reactions involving oxygen or oxygen carrying gases.

SUMMARY

Since experimental work on various phases of carburization is still in progress it would be premature to draw definite conclusions. The following points are of interest.

1. Carbonates as such are not needed as energizers in carburizing compounds. It may be that considerations of cost and con-

venience make it desirable to add energizers to the compound as carbonates.

2. There are a number of materials which will act as positive catalysts or energizers for the process of carburization.

3. There are other materials which will act to retard carburization as to case depth and carbon concentration.

4. Variations in case depth and carbon concentration as produced by different energizers are given in the tables.

5. When only pure carbon is used as a packing material a case is obtained which is very shallow and of low carbon concentration. Pure carbon can be energized by various materials, even as unlikely a one as silica.

6. When oxygen of the air is not available, i. e., when the carburizing container is swept with nitrogen, only those energizers which can be readily decomposed to yield oxygen show any effect. Under these conditions it would seem that their sole role is to produce oxygen-carbon compounds or oxygen-iron compounds.

7. No sample of carburizing compound was re-used, and hence no comparison can be made of those tested as to commercial efficiency. However, there is no reason to believe that with a proper method of binding, the energizers studied would not give repeated results of the same order as here indicated.

8. Representatives from most of the groups of the periodic system were included in the investigation. Classification of the results on this basis has been tried, but led to no conclusions except those generally known, viz., that the alkaline earth and alkali metal compounds are, in general, more effective as energizers than metals of other groups.

ACKNOWLEDGMENT

The assistance and advice of Professors R. S. Tour and R. O. McDuffie is gratefully acknowledged. The cooperation of the McQuay-Norris Mfg. Co., and Sam Tour, vice-president of Lucius Pitkin, Inc., is also appreciated.

DISCUSSION

Written Discussion: By R. R. Abbott, metallurgical engineer, White Motor Co., Cleveland.

I have been extremely interested in reading this paper of Dr. Enos. It shows much thought and careful investigation. Very little of it, however, is

new, as I believe that practically the same work carried out on a much greater scale has been done by many investigators in the United States and abroad, particularly during the years of 1907 to 1911 when the energized carburizers were being developed.

I carried out similar experiments between 1906 to 1911 using, with the exception of the oxides of boron, zirconium and cerium, and the carbide of silicon, all of the materials given in Dr. Enos' tables and in addition many other materials including the oxides of zinc, lead and copper and also innumerable salts such as sulphates, chlorides and nitrates.

It is interesting to note the use of calcium carbide by Dr. Enos, this of course was one of the first things investigated, with the idea that a carbide would lend itself to the rapid formation of cementite. About 1912 many rumors were afloat that some manufacturer of carburizing material was bringing out a calcium carbide material which would shorten the carburizing time drastically.

So much for history, may I now make a few comparisons of methods which might be helpful. In my original experiments I used the method of measuring the case depth but soon found out that this was not satisfactory as it was too difficult to make accurate comparisons. In all my experiments I used a $\frac{3}{4}$ "x $\frac{3}{4}$ " cylinder machined in an automatic lathe to give accurate sizing. These were weighed on an analytical balance before and after carburizing. By this method the exact carbon absorption was determined. The specimens were all cooled in the furnace. They were finally sawed in two and checks were made by measuring depth of the different carburized zones. I do not see the advantage of the hollow cylinder used by Dr. Enos.

The results which Dr. Enos obtained by suspending the steel samples above the carburizing compound are probably explained by the use of the small container and the small amount of material. Steel will carburize very readily if suspended in a large carburizing box above the carburizing material.

For several months in 1910 I did all the carburizing in a large automobile plant by placing 12 per cent of Na_2CO_3 in the bottom of the boxes and then packing the work above this in charcoal and in mixtures of charcoal, coke and sawdust. The work was very satisfactory. Likewise for several years I carburized all material which had to be subsequently ground in a mixture of 12 per cent Na_2CO_3 in mahogany and oak sawdust. This would shrink in volume and leave about two thirds of the work untouched by the compound and yet the results were satisfactory.

I would suggest that for accurate comparisons the test boxes should be placed on a movable piece of sheet iron in a circle and this iron revolved slowly in the furnace.

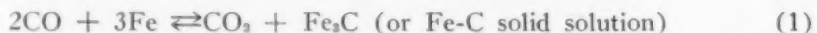
In conclusion I wish to express my admiration for the work of Dr. Enos and trust that this is only a preliminary to a more exhaustive investigation on his part.

Written Discussion: By Yap, Chu-Phay, physical metallurgist and chemist, 27 Grove St., New York City.

On account of Professor Enos' connection with the University of Cincinnati and of the participation of some of his students in the experimental work, one may legitimately infer that the paper under discussion is a piece of academic research. Therefore, as such, it is regrettable that Professor Enos

did not assign one of his students to survey the literature on the subject. Particularly unfortunate has been his ignorance of the existence of three brilliant papers by Professor Takahashi¹ of the Tohoku Imperial University, Sendai, Japan. Much of the work reported in the present paper duplicates in scope Professor Takahashi's investigations, which were, however, very systematically planned from a theoretical point of view. As Professor Takahashi's papers are easily accessible to all interested in the subject, I shall not repeat here his various conclusions.

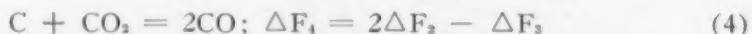
In reading Professor Enos' paper, I gather the impression that he and his associates subscribe to the general theory that the formation of CO_2 from M_2CO_3 , which in turn reacts with carbon forming CO , is the cause of more rapid carburization of iron and steel. Professor Takahashi, however, has conclusively shown that the carbonates catalyze the carburization (I do not like the word "energize") in the presence of CO gas at temperatures at which the carbonates are not dissociated at all. Moreover, in the presence of hydrocarbon gases (that is, absence of CO) the presence of the carbonates has no effect on the rates of carburization. The conclusion that the function of the carbonates is that of a catalyst seems inescapable—and here I also differ with Professor Takahashi. Professor Takahashi's mistake, it appears to me, lies in trying to match chemical equations involving kinetics or rates of reactions, with equations involving energy changes (thermodynamic equations). It should be very easy to prove or disprove my view regarding the rôle of the carbonates as surface catalysts, because the finer the carbonates are ground, the more effective they should be as catalytic agents. Personally, I think much of the confusion regarding the mechanism of carburization is attributable to the equation (1) given in Professor Enos' paper, that



because it conveys the impression that carburization is due to the interaction of the CO gas with iron. (This gives rise to the controversy as to whether carburization is caused by the diffusion of CO or Fe_3C [or carbon].) Let us analyze the mechanism of carburization. In the first place, separating his equation (2) into two parts, we have



Multiplying equation (2) by 2 and subtracting equation (3) gives



which is the equation (2) given in Professor Enos' paper. I shall not apologize to my colleagues for introducing free energy equations, because I shall show how useful they can be in clarifying certain points regarding carburization. Giving figures for the values of ΔF only in terms of kilocalories, I find that

¹G. Takahashi, "On the Mechanism of Carbon Penetration in the Cementation of Iron and Steel," "On the Energizing Action of Carbonates Contained in Carburizing Mixture," and "On the Relation Between the Quantity and the Depth of Carburization," *Science Reports*, Tohoku Imperial University, Vol. 17, 1928, p. 761, 883, 1135.

$\Delta F_{2-298} = -32.5$, $\Delta F_{3-298} = -94.3$, so that $\Delta F_{4-298} = 29.3$ Kcal. On the other hand at, say, 927 degrees Cent., I find that $\Delta F_{2-1200} = -51.7$, $\Delta F_{3-1200} = -94.3$, so that $\Delta F_{4-1200} = -9.1$ Kcal. The values of ΔF_3 are obtained from the Lewis and Randall equation,² ΔF_4 from Eastman's equation,³ and ΔF_2 by subtraction. I have given the values of ΔF at both room temperatures and 927 degrees Cent., because I want to show how the gases are likely to form upon heating up the carburizing pot from room temperature to the carburizing temperature of, say, 927 degrees Cent. Viewing reactions (2) and (3) to take place independently, CO_2 will be formed in preference to CO , but as the temperature increases, the CO_2 begins to react with carbon to form CO according to equation (4). As long as the partial pressure of CO_2 required by equation (4) is maintained, the CO gas will form directly according to equation (2). Since thermodynamics has nothing to do with rates of reaction, we do not know how rapidly reactions (2), (3) and (4) may take place. Although these reactions are uni-molecular reactions, it is difficult to evaluate individually the different rates of reaction.

At 927 degrees Cent., the CO/CO_2 mixture is of the order of 97.85 per cent CO and since CO becomes increasingly stable as the temperature increases (that is, the value of ΔF_2 becomes a larger negative quantity), CO is formed directly and also by the reaction of CO_2 in contact with hot carbon according to equation 4. Although the forward reaction in equation (4) takes place rapidly, the backward reaction (that is, to the left) is known to be very slow. I should like to mention here that an erroneous conception regarding the mechanism of carburization lies in the fact that in the forward reaction of equation (4) the solid carbon (charcoal, for example) is involved, but in the backward reaction the carbon produced is most probably nascent carbon deposited in the form of a mono-molecular layer on the iron and steel sample. This carbon then combines to form Fe_3C which diffuses inward according to Fick's law.

On the basis of this kind of evidence, Professor Takahashi has concluded that the solute in austenite during carburization is carbon and not Fe_3C . This does not appear to be justified, because I have found that the free energy of formation of Fe_3C is negative. It is outside the province of this discussion to go into details regarding the probable mechanism of diffusion of Fe_3C .

Hence, any catalyst (e.g., even metals like nickel and cobalt) which will accelerate the decomposition of CO to $\text{CO}_2 + \text{C}$, will consequently increase the rate of carburization. Here, Professor Takahashi and I differ, because he maintains that the catalytic action is due to the decomposition of the carbonates and the subsequent reaction between the oxide and the CO gas according to the following equation



while by the action of CO_2 gas, we have



²Thermodynamic and the Free Energy of Chemical Substances. New York, 1923. McGraw-Hill Book Co.

³Information Circular 6125, Bureau of Mines, May, 1929, pp. 11-12.

Now according to free energy calculations above, we see that reaction (6) is more likely to take place than reaction (5) because the decrease in free energy in the former is larger than in the latter. This is merely tantamount to saying that the free energy change of equation (5) minus equation (6) giving equation (4) (reversed) is positive. In Professor Takahashi's case, when he starts with pure CO gas, naturally he obtains carbon, deposited on the carbonate thus formed. If his conception regarding the rôle of M_xO is correct, then those carbonates which dissociate easily at lower temperatures, or better still, the simple oxides, should prove to be the best catalysts. This is, however, not supported even by his own experiments. The oxides apparently act as catalysts simply because in the presence of CO_2 gas, they form the carbonates again. Those carbonates which have low CO_2 dissociation pressure should be more active as catalysts.

In order not to complicate my discussion too much, I have refrained from introducing the concepts of activity, partial molal quantities, standard states, etc., although a more rigorous thermodynamic expression of equation (1) should be



as we do not have pure γFe in contact with Fe_3C , but γFe (containing x mol of Fe_3C) the activity of which is a' . I hope to treat these topics at some length in my forthcoming paper on the free energy and heat of formation of Fe_3C from room temperature to 1400 degrees Cent.

Since this was written, I have had the pleasure of discussing with Professor Enos the background of his paper and in justice to him, I should like to say that his efforts are in the right direction and that he deserves great credit for the work represented in his paper. I should, therefore, like to congratulate him.

Written Discussion: By R. A. Ragatz, assistant professor of chemical engineering, University of Wisconsin, Madison, Wis.

Dr. Enos has made an interesting contribution to our knowledge of the energizing effect exerted by various chemicals in the carburization of steel with carbonaceous materials.

The writer is unable to accept the tentative theory offered by Dr. Enos to explain the mechanism of the action exerted by energizers. According to the proposed explanation, intermediate carbides are formed which act as carriers for the carbon. This theory is not in accordance with the following facts: (1) Carbides such as barium carbide are difficult to form and are essentially high temperature products produced only at temperatures far in excess of those used in carburization. (2) The writer has found that barium and calcium carbides are poor energizers. The former exerts a slight energizing effect, but is not nearly as effective as barium carbonate. Calcium carbide is entirely inert. Dr. Enos has also reported that silicon carbide is practically inert. In view of these facts, the theory proposed appears to be untenable. As a result of an extensive series of tests carried out by O. L. Kowalke and the writer, a somewhat different theory has been developed to explain the mechanism of energizer action. A proper presentation of this theory is not possible at this time, but will probably be published in the near future.

There are two points respecting the experimental procedure upon which

the writer would like to have Dr. Enos' comments. (1) The charcoal passed 8-mesh and rested on 35-mesh screen. It would appear that under these conditions considerable difficulty would be experienced in incorporating the energizer uniformly with the charcoal. There would appear to be considerable opportunity for segregation of the energizer to occur. (2) It is stated that some 30 to 40 containers were treated at one time. Was the temperature uniformity adequate to insure uniform treatment for all of the specimens? In reviewing the data, it is apparent that considerable divergence exists between maximum and minimum values. Might not these variations be due to the two factors mentioned above?

Written Discussion: By Hugh Rodman, general manager, Rodman Chemical Company, Verona, Pa.

By successfully using oxides instead of carbonates Professor Enos again demonstrates the comparative unimportance of the CO_2 portion of the usual carbonate energizers. This fact may be arrived at in another way. When carburizing compound containing alkali or alkali-earth carbonates is heated, the carbonates quantitatively reduce to oxides and these absorb carbon dioxide and reform carbonate only slowly when the compound is subsequently exposed to air. If the used compound is repacked with fresh steel before appreciable absorption of carbon dioxide occurs, effective carburization is secured. That is, the oxide energizer functions quite as well as the original carbonate energizer.

Professor Enos swept his hot compound with nitrogen during a carburizing heat, found no carburization and suggested making the same demonstration by vacuum method. I have effectively stopped all carburization by connecting the carburizing pot by pipe with a vacuum pump. The pot was gas-tight except for the pipe, was packed with a commercial compound and was heated for several hours at the usual temperature.

Professor Enos questions the carburization of steel by direct deposition of carbon from gas. Two strips of steel, one a quarter inch thick and one a few thousandths thick, but having the same area, packed in the same box, will gain equally in weight. The thick strip will have a clean surface while the thin strip will have a deposit of loosely adherent carbon resembling soot. Apparently carbon deposition occurs in each case and the carbon is absorbed or not absorbed according to the capacity of the steel to do so.

Most of Professor Enos' mixtures were made by adding chemicals to ordinary wood charcoal, a form of carbon carrying an effective amount of alkaline ash. His results must therefore be interpreted as indicating the effect of mixtures of chemicals rather than the effect of any individual chemical. This of course does not lessen the importance of his observations upon the effect of chemical additions to this important type of carbon, but it does lessen the ease of interpretation of the effect of the chemicals when added to inert carbon. As an example of this difficulty, Professor Enos finds silica a mild positive energizer when mixed with sugar char and a decided negative energizer when mixed with wood charcoal. The truth seems to be that silica is practically ineffective as an energizer but does to some extent neutralize the alkaline ash in the charcoal. This observation applies to many of the chemical additions to charcoal and to commercial carburizing compounds; they seem to be merely catalyst poisons, not energizers.

The tests with titanium oxide (Table III) looked interesting until the arithmetical error was seen. Professor Enos has apparently figured the case depth as equal to the total thickness of the cylinder wall of the test piece, whereas the depth could obviously not have been over half that. The same error is repeated in reporting the case depths obtained with commercial carburizing compounds. (Table I.) The correct findings for titanium oxide are indicated in Table VII where a 10 per cent addition of titanium oxide is ineffective. The results for 15 per cent are evidently errors from Table III.

The results obtained by Professor Enos in testing mixtures of charcoal and 15 per cent of alkali or alkali-earth carbonate or oxide (see Tables II and III) are not in agreement with my past experience in testing similar mixtures. Professor Enos finds magnesium carbonate more effective than calcium carbonate and magnesium oxide as effective as barium oxide. He also finds his charcoal and barium carbonate mixture less effective than commercial compounds.

As a check upon these differences in observations, I attempted to duplicate Professor Enos' mixtures and also prepared similar mixtures using pitch coke instead of charcoal. These mixtures were packed in the usual way, but in somewhat larger pots than were employed by Professor Enos. The results indicate that magnesium is practically ineffective with either type of carbon, that calcium is more effective, that the barium mixtures are as effective as commercial compounds. The original mixtures were made with carbonates. As these reduce to oxides when heated with carbon, the active energizer is evidently the oxide, not the carbonate. However, in order to make sure that the original carbonate condition had no bearing upon the results, the used compounds were repacked with fresh test pieces without allowing time for any appreciable amount of CO_2 to be absorbed, and the test was then repeated. The results were the same as before. That is, magnesium was practically ineffective, calcium was moderately effective and the barium mixture was as effective as commercial compounds. These results were obtained by determining the gain in weight of the test pieces, not by observation of surface carbon and case depth, but it seems to be established that gain in weight, case depth and surface carbon rise and fall together under identical conditions of time, temperature and type of steel.

I have heretofore reported upon a series of tests made to determine the relative effectiveness of the several alkali and alkali-earth carbonates when used as energizers in carburizing compounds.⁴ In these tests some difficulty was found in correlating the results obtained when charcoal was used (because of its alkali content) and also when ordinary coke was used (because of its silica content) but the results obtained when pitch coke was used fell into a definite order. These results are indicated below as relative energizing effects, the effect with barium carbonate being arbitrarily fixed as 100.

Lithium	110	Magnesium	15
Sodium	70	Calcium	43
Potassium	57	Strontium	79
		Barium	100

⁴Hugh Rodman, "Specific Effect of Alkalies in Carburizing Compounds," *TRANSACTIONS, American Society for Steel Treating*, Vol. 7, May, 1925, p. 635.

Apparently the energizing effect follows the order of the atomic weights, directly in the case of the alkali-earths and reversely in the case of the alkalis.

In seeking an explanation of the differences between Professor Enos' results and my own, I am inclined to believe his results were affected by the very small size of pot he employed (one-fourth pint size), which necessarily brought his test pieces near the top of the compound. Any leakage of furnace gases during the carburizing heat or the cooling off period would probably influence the results, especially the degree of surface carburization. It is also probable that the use of coarse energizer (8-mesh and less) in some cases and finely powdered energizer in other cases may have caused some of the extremely nonuniform results to which Professor Enos refers. It is customary to make commercial compounds with finely powdered energizers and it is my belief that this is necessary for best results, especially when non-fusing energizers are used. I believe Professor Enos' paper must be read with these reservations in mind.

Professor Enos' paper deals principally with the effect, rather than with the rôle, of energizer additions to carbon. It would be interesting to have a paper upon the rôle, that is, the actual *modus operandi*, of the energizer addition. Apparently our best guess at present is that the alkali or alkali-earth oxides act as catalysts in the presence of carbon to facilitate the reduction of CO_2 to CO. The CO floats over to the steel, which acts as a second catalyst to bring about deposition of carbon and formation of CO_2 . The CO_2 floats over to the energized carbon and is again reduced to CO. The deposited carbon is absorbed by the steel, or not, according to circumstances. Additions of silica, silicates, etc., to the compound may poison or neutralize the alkaline catalyst and lessen its effectiveness.

Written Discussion: By O. W. McMullan, metallurgical department, Timken-Detroit Axle Co., Detroit.

A number of experiments were made in the Timken-Detroit Axle Co. laboratory last January which confirm some of the results found by Dr. Enos. The solid mixtures tried consisted of coke from coal and about 20 per cent of the "energizer." Coke alone gave no case.

Mixtures with BaC_2O_4 , BaCO_3 or BaO gave good cases, the latter being best. Mixing of the energizer is not necessary to produce some case. When BaO was placed in the bottom of the container and the sample packed in coke above it, a saturated case was produced. A similar run with BaCO_3 produced a much shallower case of low carbon content.

Mixtures with Fe_2O_3 , Fe_3O_4 , or ZnO produced no appreciable case. MgO mixtures produced considerable case but of hypoeutectoid content. Dolomite mixed with coke and a small amount of molasses gave a good case with some excess carbide.

A few experiments were made to determine the rôle of the gases in carburizing. Oxygen was passed through coke in a sealed tube heated in an electric furnace to 1700 degrees Fahr. It was thought that by obtaining the right flow that carbon dioxide and monoxide would be obtained as with solid carbonate energizers. No case was obtained either by intermittent or continuous flow of oxygen in any quantity. Sufficient time was not available to finish these experiments or to make the proper gas analyses. On the other

hand, the mere presence of the barium radical does not constitute an energizer as a mixture of coke and BaCl_2 gave but a slight case.

Author's Closure

We were of course aware of the results obtained by Mr. Rodman (see footnote 4); and reference was made to this paper in the report on the earlier portion of our work. Mr. Rodman's comments are of value, and a reply on my part is not needed except on a few points. In Table III, in the preprint of the paper the variation in case depth for titanium oxide as an energizer was stated to be from 0.159 inch as a maximum to 0.015 inch minimum. Again in Table I the same numerical error occurred. If the word "complete" is substituted for the value 0.159, a true conception will result. 0.159 inch is the average wall thickness of the hollow cylinders used in the test. With reference to the 15 per cent addition of titanium oxide to wood charcoal, seven runs were made, of which one gave but little case and one was completely carburized. Only hypoeutectoid cases were obtained on these runs. Taking the five runs which checked closely, the actual average case depth was 0.037 inch and the carbon concentration average was 0.6 or 0.7 per cent.

In considering the relative effects of barium and magnesium compounds (carbonates and oxides) I can only say that I have checked over the measurements made and find, as reported, that the magnesium compounds give a fairly deep case, as deep as the barium compounds, but that the carbon concentration is less when magnesium compounds are used.

With regard to the size of containers and method of incorporation of energizers, it is of course possible that nonuniform results, and nonagreement with Mr. Rodman's results can be traced to this cause. I believe that the carburization should be independent of the container and the exact amount of carburizer used, and also of the method of incorporation of the energizer with the carbon base. Mr. Abbott has covered this latter point in mentioning how carburization was carried out with energizer at the bottom of the pot. It is possible that slight decarburization occurred in some of the cans during the cooling period. We took precautions to cool all heats as uniformly as possible, both as to furnace atmosphere and rate of temperature drop.

Mr. Ragatz mentioned the matter of temperature uniformity in the furnace. The furnace used was explored by suitable thermocouples before it was used, and found to be very uniform as to temperature. Likewise, as far as possible, the furnace was explored during different heats, and no serious temperature differences were found to exist. It is true, as Mr. Ragatz suggests, that the energizer might not be incorporated uniformly with the base. It is our belief that except where mechanical loss of the energizer might occur on handling between heats, that the exact distribution and binding of the energizer is unimportant. See Mr. Abbott's comments.

We are not ready to develop in detail, with experimental proof, the validity of the suggested equations for the mechanism of carburization. We have presented these equations as an example of how the catalysis might be expected to work. In an explanation of this kind it is not necessary to postulate the forma-

tion of appreciable amounts of barium carbide nor is it certain or essential that the carbide, BaC_2 is the one formed. There may be other carbides formed at carburizing temperatures.

Mr. McMullan's discussion is very interesting and I am glad that his experimental work is in agreement with ours on the points mentioned. Mr. Abbott's comments are interesting and valuable. We were aware, of course, that considerable experimental work had been done in the past.

The number of papers dealing with the various phases of carburization is extremely large. Our thanks are due to Mr. Yap for calling our attention to the work of Prof. Takahashi and for discussing it at this time. The men associated with me in this work compiled quite an appreciable bibliography of both theoretical and practical articles. Obviously a historical review of the work of all other investigators was not attempted in preparing this paper.

Mr. Yap is in error in his impression that we subscribe to the theory that the formation of CO_2 from MxCO_3 , the CO_2 being a source of CO , is the cause of more rapid carburization. We have attempted to show that a carbonate, as such, is not necessary. Mr. Potter and the writer have confirmed Mr. Rodman's earlier work in this respect. On repeated runs with commercial compounds, it was shown that the energizers do not completely regenerate to form carbonates. (This report will appear in *Metal Progress*.) We believe that the energizing effect of the additions of carbonates is due to the compounds left after CO_2 has been evolved. We have suggested a possible mechanism for the catalytic effects. Obviously it would be premature to claim that this is the true explanation.

In Mr. Yap's excellent discussion of the mechanism of carburization (which of course should be read in comparison with the papers by Prof. Takahashi) he considers carburization from a viewpoint which is different from that ordinarily employed. Without questioning the numerical values which he gives, I would like to point out that Mr. Potter and the writer were unable to find any evidence of appreciable amounts of carbonates, as such, in commercial carburizing compounds after carburizing. I cannot subscribe to the view that the oxides function as catalysts simply because in the presence of CO_2 gas they form carbonates. Our experimental evidence in this connection will appear in *Metal Progress*.

THE CHARACTERISTICS OF DEFORMATION OF STEEL UNDER CONSTANT LOAD AT ELEVATED TEMPERATURES

BY G. R. BROPHY

Abstract

The characteristics of deformation under increasing loads and constant loads have been studied over a wide range of temperatures for several steels. As a result three types of steel are recognized.

(1) Those which show more or less sudden yields above the proportional limit from room temperature up to some elevated temperature, above which the yielding becomes smooth.

(2) Steels which show smooth load-deformation curves at room temperature and at high temperature, but at intermediate temperatures the curves are stepped.

(3) Those which show smooth curves at all temperatures.

The influence of heat treatment on these diagrams; and heat treatment and pre-straining on time-deformation diagrams are discussed.

The idea is presented that creep is a strain hysteresis which may be mathematically predicted for long periods from tests conducted for only a few hours.

THE need for a relatively short-time test to determine the deformation characteristics of steel at elevated temperatures has been felt for some time, and such a test is now particularly desirable with the large number of newly developed steels to be tested.

Attempts have been made, but the great difficulty has been to determine accurately, for design purposes, the extent of the total deformation in the life of the structure under consideration. Even with the present methods of long time tests the results can be given with accuracy only for the period of the test.

The purpose of the present paper is not to give quantitative design data, but to present qualitatively results of a study of the

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, G. R. Brophy, a member of the society, is associated with the research department of the General Electric Co., Schenectady, N. Y. Manuscript received May 2, 1931.

fundamentals of deformation and to suggest a possible short-time method for consideration and, undoubtedly, discussion.

The apparatus used and the methods followed are essentially those used and described by Professor Albert Sauveur¹, with changes

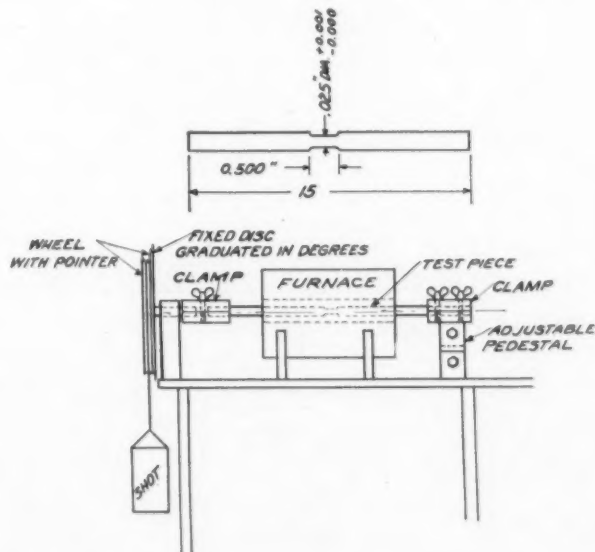


Fig. 1—Diagram of Apparatus Used in Tests.

in methods of taking data to suit our purposes. A sketch of the apparatus and test bar used is shown in Fig. 1.

It was found in our experiments that among the steels investigated, three types could be recognized as having load-deformation curves of different characteristics. Type I, shown in Fig. 2, has a stepped diagram (as found by Sauveur and others) up to some elevated temperature, and above that temperature, a smooth curve. As the temperature increases above room temperature, the number of steps decrease², but each step increases in magnitude and of course the so-called plastic portion of the curve is displaced downwards. This type of curve is characteristic of annealed simple low carbon steel.

A second type, shown in Fig. 3, is characteristic of quenched, and quenched and tempered simple steels and of some alloy steels. Smooth load-deformation curves are obtained at room temperatures

¹Prof. Albert Sauveur, Campbell Memorial Lecture, "Steel at Elevated Temperatures," TRANSACTIONS, American Society for Steel Treating. Vol. 17, 1930, p. 410.

²Yuasa reports an increase in the number of steps up to 200 to 300 degrees Cent. having found as many as 1500 steps in some steels at this temperature. *Journal of the Faculty of Engineering, Toyko University*, Vol. XVII, No. 9, March, 1930.

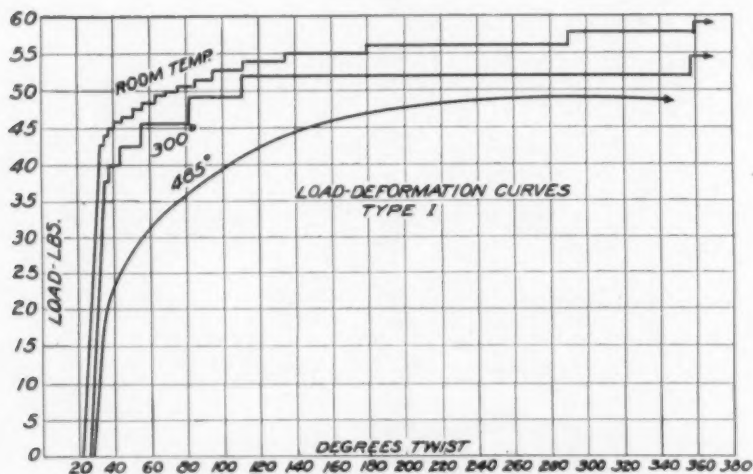


Fig. 2—Curves Characteristic of Annealed Simple Steels.

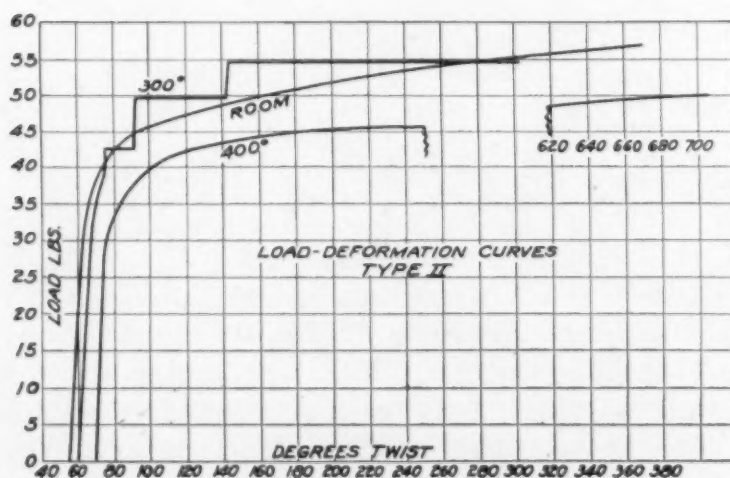


Fig. 3—Curves Characteristic of Heat Treated Simple Steels and Some Annealed Alloy Steels.

and at higher temperatures; but at intermediate temperatures, steps are found as before.

The third type, shown in Fig. 4, shows smooth load-deformation curves from room temperature up. As stated by Sauveur, this curve is characteristic of austenitic steel.

The curves shown in Figs. 2, 3 and 4 do not show the time element, so it might appear that in all cases a step is a sudden deformation. Our observations indicate that each step, whether a quick sharp twist or a slow one, starts off slowly, and quickly accelerates to a maximum and then decelerates and finally stops.

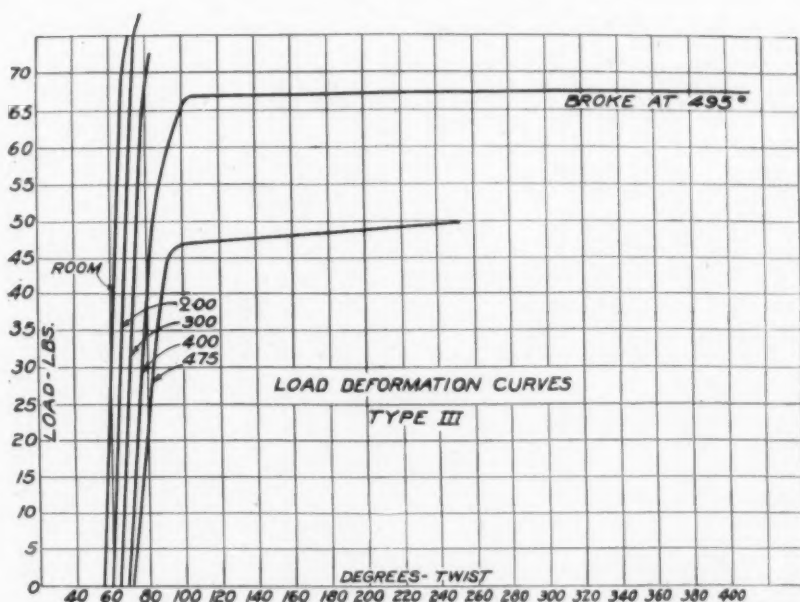


Fig. 4—Curves Characteristic of Austenitic Steels.

Fig. 5 shows a stylus diagram of a single step which may be considered characteristic. That deformation ceases is proven by the fact that the load was left on this sample for forty-eight hours and no measurable further deformation took place.

It was found that those steels which show a stepped load-deformation diagram lose the steps at some elevated temperature and that this temperature varies from 375 to 475 degrees Cent. (705 to 890 degrees Fahr.) for the steels tested.

Van Wert³ believes that the steps are caused by the rapid apparent elastic recovery at elevated temperatures through the mechanism of dispersion hardening. The hardener, in his opinion, is nitride, oxide, or carbide. In this idea the author concurs, and the results of the following experiments lead to the same conclusion.

An alloy steel was tested at a temperature of 475 degrees Cent. (890 degrees Fahr.) which was about the temperature at which steps disappeared in the annealed steel. Four conditions of heat treatment were used. One set of samples was thoroughly annealed, and a second set was water-quenched from 800 degrees Cent. (470 degrees Fahr.). The other two were quenched and then tempered at 400 and 600 degrees Cent. (750 and 1110 degrees Fahr.).

Fig. 6 shows the time-deformation curves for these samples for

³Technical Publication No. 404, American Institute of Mining and Metallurgical Engineers, 1931.

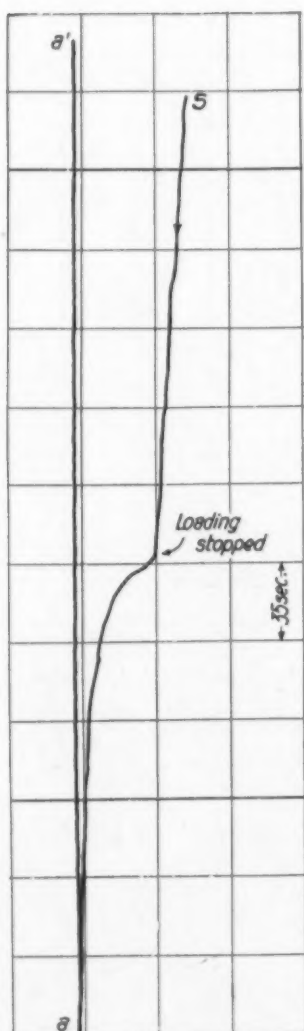


Fig. 5—Stylus Diagram of a Single Deformation Step Such as is Shown in Figs. 2 and 3.

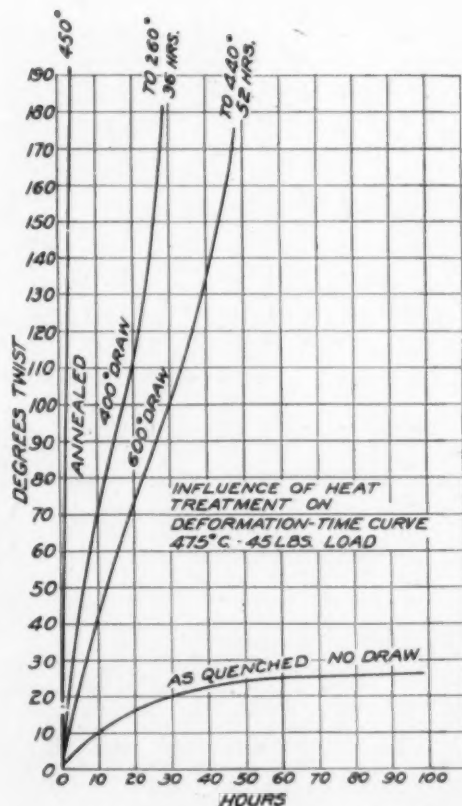


Fig. 6—Curves Showing Influence of Heat Treatment on Deformation-Time Curve at 475 Degrees Cent. and 45 Pounds Load.

a load of forty-five pounds. The annealed material had little resistance and failed quickly after twisting 475 degrees Cent. (890 degrees Fahr.).

The quenched condition was the most resistant and apparently hardened under the influence of stress and temperature quickly and effectively.

At first glance it would seem that the two tempered samples are out of order, but by reasoning that the dispersion of a hardener from solid solution is responsible for the stiffness, then the order is logical.

If we assume, for instance, that the temperature for complete solubility of this hardener is somewhere between 500 and 600 degrees Cent. (930 and 1110 degrees Fahr.) the quenched sample and that tempered at 600 degrees Cent. (1110 degrees Fahr.) and air-cooled can be considered solid solution alloys with respect to the hardener. The annealed sample, of course, would contain the hardener in a completely precipitated condition and of large particle size, in which

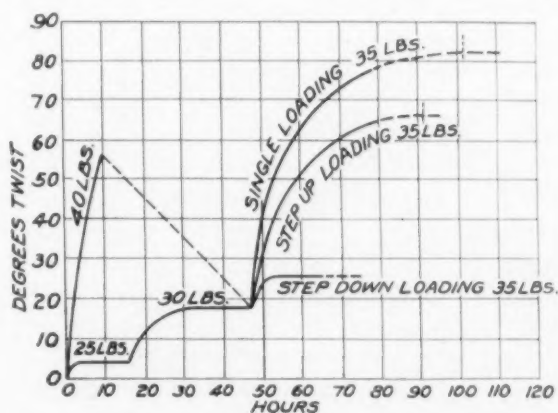


Fig. 7—Influence of Previous Straining on Strain-Time Diagrams.

condition it would be least effective as a stiffener. The sample tempered at 400 degrees Cent. (750 degrees Fahr.) would not have the hardener so completely precipitated nor of such large particle size so that it would be stiffer than the annealed condition.

It is generally believed that, at temperatures where precipitation will take place, precipitation under stress, as a stiffener, is more effective than when stress is absent. Therefore, the two solid solution conditions (quenched and 600-degree Cent. temper) would be stiffer than the steel in the two precipitation conditions (annealed and 400-degree Cent. temper).

As previously stated, a temperature was reached below which, in some steels, stepped load-deformation diagrams were obtained, and above which smooth diagrams were obtained. This temperature we have chosen to call the "strain hardening temperature limit" and it marks the temperature at which the annealing effect overcomes the strain hardening effect. It is believed that below this temperature all deformation under constant load will cease. Above this temperature deformation will more or less quickly lead to failure. It follows, therefore, that at but a single temperature, where the an-

nealing effect just offsets the strain hardening effect, can deformation proceed at a constant rate.

It is to be expected that previous straining will influence the load-deformation diagram of a steel and the following experiments were conducted to determine this influence. A steel was chosen which had

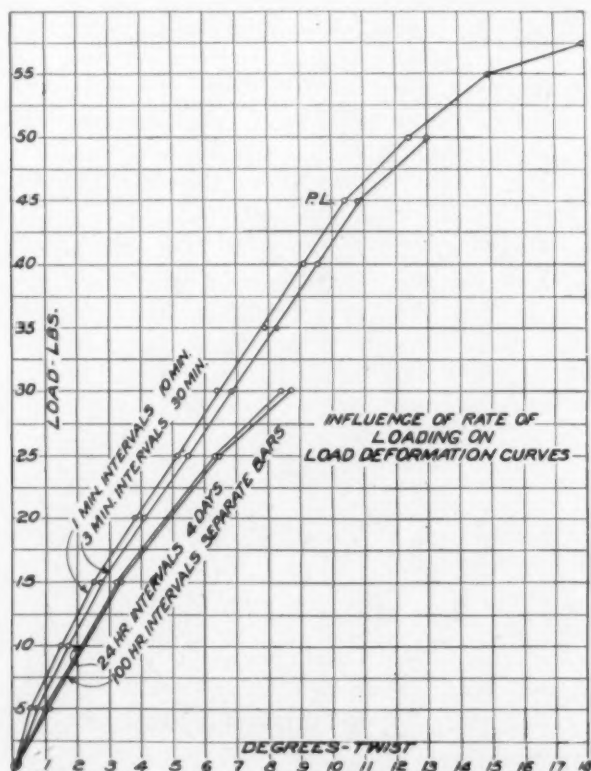


Fig. 8—Influence of Rate of Loading on Load Deformation Curves.

a strain hardening temperature limit about 450 degrees Cent. (840 degrees Fahr.) and strained by a final load of thirty-five pounds. This load, however, was arrived at by three methods of loading. First, a single load of thirty-five pounds was applied and the load-deformation diagram plotted. Fig. 7. Another bar was first loaded with forty pounds for the time indicated on the diagram and then the load reduced to thirty-five pounds. A third bar was loaded with twenty-five pounds, then thirty pounds, and finally thirty-five pounds.

It is interesting to note that the total deformation, regardless of the method of loading, remains about constant when the curves are extrapolated to zero rate. If a determination of a rate (other than

zero) was attempted from these curves, decidedly different rates would be obtained which, for the same steel at the same temperature and load, is anomalous.

Up to this point in the experiments the loads used were all in excess of the indicated proportional limit or in the region where steps occurred. So, it was decided to work with smaller loads and also to study the influence of rates of loading, since indications had

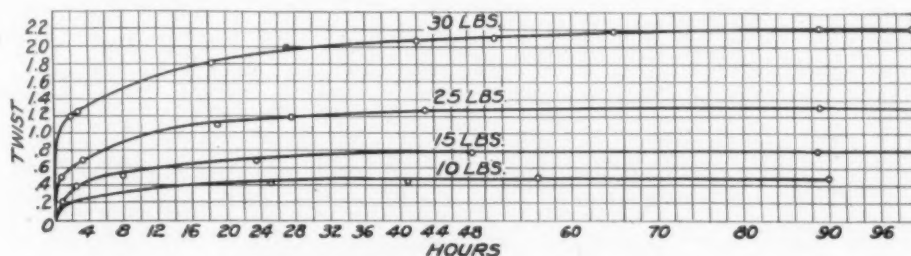


Fig. 9—Time-Deformation Curves by Twisting.

been obtained that the deformation with time was perhaps an hysteresis effect, or an "elastic after effect" as some writers term it.

Load-deformation diagrams were determined for an alloy steel at 450 degrees Cent. (840 degrees Fahr.) for different rates of loading. The temperature was determined by experiment to be just within the strain hardening temperature range for the thoroughly annealed steel. Bars were loaded to just beyond the indicated proportional limit by rapid loading and the data plotted. The usual elastic and plastic portions of the curves are indicated. Fig. 8. Fairly good checks were obtained when the time of loading was within a half hour. When, however, the bars were loaded by increments every twenty-four hours, a much lower modulus is indicated by the slope of the elastic portion of the curve and the proportional limit is found to be considerably lowered. This method of loading (step up) was repeated, but this time three load increments at forty-eight hour intervals were applied and a diagram obtained which differed but slightly from the previous one.

The deformation interval between the most rapid and the slowest rate of loading represents what is believed to be the hysteresis mentioned above, and it is probable that this approximates the total "creep."

Four bars were separately loaded at 10, 15, 25, and 30 pounds and the time-deformation curves obtained over a period of 100 hours.

In each case the deformation approached a limiting value. Fig. 9. Whether this limit was reached or not, can only be determined by greater accuracy than was at our disposal.

Plotting the difference in distortion between the end of the loading period and the 100 hour period, a load-deformation diagram

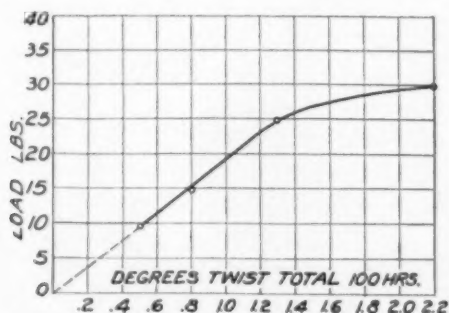


Fig. 10—Deformations Obtained in Fig. 9 Plotted Against Load.

is obtained which practically coincides over the elastic portion with the long interval "step-up" curve.

This result supports the idea that "creep" and elastic hysteresis, if not the same, are closely related. It is to be understood that this probably holds only within the strain hardening range and for loads within the proportional limit for the rate of loading and the temperature of test.

A mathematical study of the time-deformation curves of Fig. 9 may lead to the conclusion that two effects are at work, from the fact that, to the flatter portions of the curve, one formula can be applied, but the steeper portion requires a second. Also, it is possible to determine mathematically the limiting deformation values which the curves approach, and to use these values as the total deformation values for the temperatures and loads under consideration.

DISCUSSION

Written Discussion: By Dr. Albert Sauveur, Gordon McKay Professor of Metallography and Metallurgy, Harvard University, Cambridge, Mass.

It is gratifying to me that Mr. Brophy could have put to such good use the simple twisting machine developed in the metallurgical laboratories of the Harvard Engineering School. I believe that in many respects the twisting test is superior to the tensile test so universally used.

In the Campbell lecture, to which the author refers, I have mentioned the possibility of rapid twisting tests replacing the slow and expensive method at

present generally used to determine the "creep" of steel. A number of steels which had been subjected to the long "creep test" by Professor Norton at the Massachusetts Institute of Technology were twisted by us at the temperatures used by him and we obtained practically the same order of value for the different steels, differentiating sharply as he had done between the nickel-chromium austenitic steels and the nonaustenitic steels. It would, I think, add to the interest of the paper if the author would give us the composition of the steel he studied.

It is rather unexpected that a steel quenched and drawn at 600 degrees Cent. (1110 degrees Fahr.) and, therefore, less stiff and less hard than the same steel drawn at 400 degrees Cent. (750 degrees Fahr.) should, nevertheless, exhibit greater stiffness and greater strength when twisted at 475 degrees Cent. (885 degrees Fahr.). The explanation offered by the author should be accepted only with reservation pending more positive knowledge of the precipitation phenomenon and its mechanism.

In accounting for the disappearance of the "steps" in the time-strain diagrams of certain steels on reaching what the author terms "strain hardening temperature limit," he appears to consider it chiefly an annealing effect. If it were so, there is no reason why stepped curves should not be obtained in chemically pure metals or at least in metals free from precipitating matter. On the assumption that the phenomenon results from precipitation, on the contrary, pure metals, obviously, should have smooth curves at all temperatures which I believe has been confirmed by our experiments. When steel is cold-worked at room temperature, it develops an urge to age due possibly to lattice distortion. This aging is assumed to result from precipitation of oxides, nitrides or carbides. Owing to the great rigidity of steel at room temperature, however, aging proceeds very slowly. On deforming the steel at higher temperatures while the deformation is less, the greater plasticity permits a more rapid aging. On deforming steel in the blue heat range, the plasticity is such that aging (precipitation) follows deformation immediately, hence the steps. On deforming at higher temperatures while aging is favored the deformation is too slight to cause precipitation, hence the smoothness of the curves. I am presenting this conception of aging and of the blue heat phenomenon in the hope that it may be of interest to some.

Written Discussion: By J. J. Kanter, Metallurgical Department, Crane Company, Chicago.

It is of considerable interest to learn through Mr. Brophy's paper that the characteristics of steel deforming under constant load in torsion resemble those that have been found through creep testing in tension. Mr. Brophy's work serves to emphasize that limiting creep stresses based upon so-called rate of creep determinations are not concise constants. It has been shown in tension as well as through Brophy's work that at temperatures just above the strain hardening range there is a tendency for deformation under constant load to reach a limit, sometimes after considerable creep has occurred. It furthermore is well known that previous straining decreases the amount of deformation taking place under subsequent conditions. This fact is emphasized by the step loading tests shown in Figs. 1, 2 and 3. It is quite evident

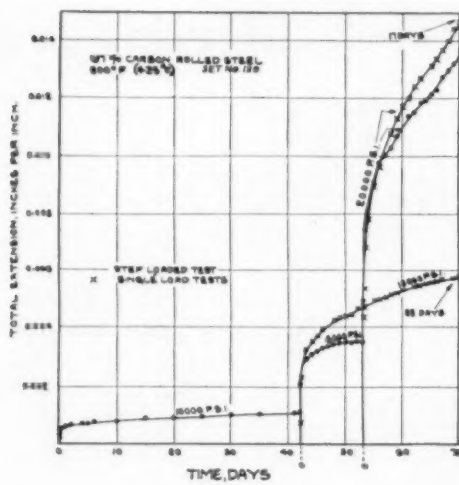


Fig. 1

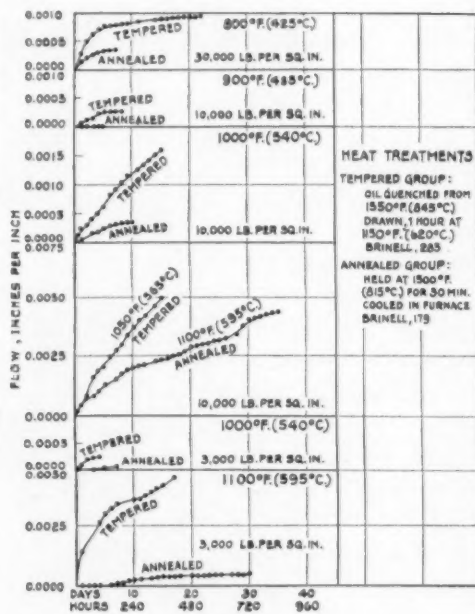


Fig. 4

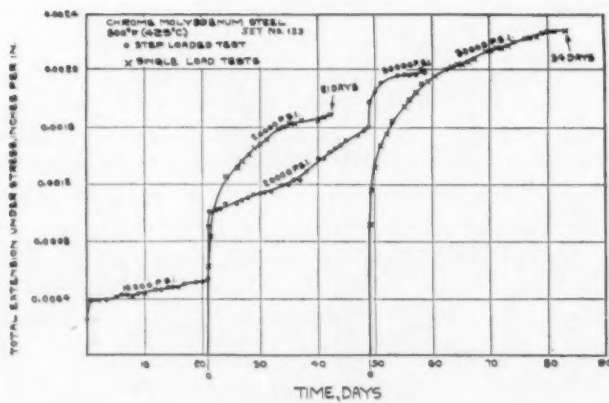


Fig. 2

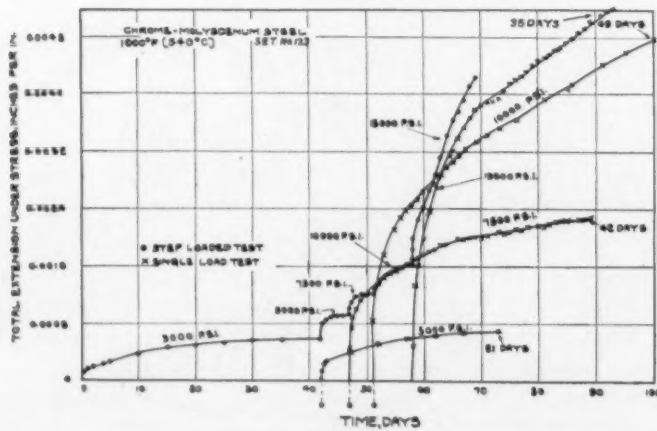


Fig. 3

from these tests that a different amount of primary creep ensues upon single loading than obtained under step loading conditions. It is not to be concluded from tension creep tests, however, that the total creep which takes place under step-up loading is equivalent to that found for single loading, although it roughly approximates it.

There is a marked tendency for the deformation under single loading to be somewhat greater than found for step-up loading. This possibly may be accounted for by change which takes place in the structure of the steel during the test. It is quite well known that a tempered steel shows considerably more primary creep than an annealed steel or another tempered steel in more stable condition. This is illustrated by the tests represented in Fig. 4, where the flow-time curves for annealed and tempered chromium-molybdenum steel are compared under various creep conditions. It will be seen that over a range of temperature from 800 to 1100 degrees Fahr. (425 to 595 degrees Cent.) and a range of stress from 3000 to 30,000 pounds per square inch, the tempered steel shows considerably more primary creep than the annealed steel. This suggests that steels in unstable conditions of heat treatment are predisposed to primary creep under constant load when at temperatures above the strain hardening range. During the creep test of a tempered steel, primary deformation seems to occur simultaneously with softening through drawing. When the draw effect approaches completion, the rate of creep seems to diminish almost to a negligible value at stresses which do not give rise to an appreciable secondary rate of flow. In the annealed steel very little thermal structural change can take place and as a result no decided primary creep is observed. It seems quite reasonable to assume that in step-up loading a tempered steel, due to the additional drawing time under small stresses, the later primary creep at the higher loads is not as large as it is when the stress is applied immediately. Upon this assumption it is reasonable to expect a somewhat greater total deformation in single loading than step-up loading.

It would be of interest to know the heat treatment of the material used for the tests shown in Brophy's Fig. 7. If the argument in the foregoing paragraph be true, these tests should be representative of annealed material or at least material given a thorough draw treatment.

Such considerations as have been set forth argue for the expression of creep stresses in terms of total deformation rather than creep rates. It previously has been advocated¹ that values of 0.1, 1 and 10 per cent total deformation per 10,000 hour period be accepted as practical tension creep stress units. At temperatures where strain hardening is a considerable factor, creep of course ceases long before 10,000 hours has elapsed. At temperatures where creep is continuous it, of course, is important to be discriminating about the amount of total creep taken as criterion.

Written Discussion: By A. E. Laverne, mechanical engineer, Edward G. Budd Manufacturing Co., Philadelphia.

I have read Mr. Brophy's paper with a great deal of interest. It seems to me that Mr. Brophy's paper lacks in some experimental details which are

¹J. J. Kanter and L. W. Spring, "Some Long-Time Tension Tests of Steel at Elevated Temperatures," *Proceedings, American Society for Testing Materials*, 1930.

necessary to understand clearly the graphs. I should like to ask Mr. Brophy:

- (a)—In what manner was the lead shot poured into the bucket? Fig. 1.
- (b)—How did he ascertain that the rate of loading (increase in load per unit time), if any, was constant?
- (c)—In cases where the bars were loaded by increments, how were these increments of load applied? Was there any determined rate of loading per increment?
- (d)—How was the load recorded to such accuracy to enable him to plot load-twist diagrams?
- (e)—Referring to Figs. 2, 3, 4, I should like to ask Mr. Brophy if the rate of loading was the same for bars of the same material but tested at different temperatures.

I should like to express some thoughts on the deformation of steel.

The method of deforming steel chosen by Mr. Brophy, although very adaptable to obtain experimental data, seems to be one which offers data which is not very easily interpreted.

It seems that torsion does not easily lend itself to interpretation. In torsion not all the cross-section is subjected to a uniform stress, but only an infinitesimal fibre. This stress differential would naturally bring into play another unknown, which may or may not play an important rôle.

Considering deformation under torsion I shall discuss:

- (a)—The inertia effects due to the appreciable static load used for producing deformation.
- (b)—The steps shown in Mr. Brophy's graphs.

When testing above room temperature:

- (a)—Deformation proceeds elastically until the yield point of the most stressed fibre is reached. At this load (assuming a strength differential to warrant the formation of steps, or, in other words, the abrupt increase in angle of twist) inertia losses would play a very important rôle. If the tests were conducted as described by Professor Sauveur in the Campbell Memorial Lecture, the magnitude of such increase of twist is quite great, at times reaching perhaps 45 degrees of twist in approximately two seconds. The magnitude of torque required to produce deformation would be in the neighborhood of 100 inch pounds. Such magnitudes of load and twist would undoubtedly cause large inertia losses, namely:

- (1)—Momentary decrease of the load sustained by the specimen. Such decrease in load may be quite large, and depending on the magnitudes of load and twist, it may at times produce an almost complete absence of the torque. This absence of torque will undoubtedly allow an appreciable length of time during which work-strengthening of the slipped planes may occur. Possibly work-hardening occurs at very high velocities when at temperatures near the blue heat range of iron.

- (2)—An acceleration of the falling bucket containing the lead shot would strain the specimen undergoing test beyond the actual static load represented by the lead shot within the bucket.

Such series of falls and arrests would furnish stepped diagrams. However, this inertia effect can only occur after the abnormal twist has begun; in other words inertia offers an explanation for the continuation of the steps but not for its origin.

- (b)—A very successful attempt to explain the cause of stepped diagrams has been made by Leland Russell van Wert.²

There is no reason to believe that the steels used by Mr. Brophy in his investigation contained abnormal amounts of oxygen or nitrogen in solution; hence there should be no appreciable precipitation effect at room temperature.

It should be noted also that Professor Sauveur gives no evidence of stepped time-strain diagrams in any of the plain carbon steels tested at room temperature and reported in the Campbell Memorial Lecture of 1929.³ Are such steps not largely due to a different manner of loading?

Oral Discussion

A. V. DEFORREST:⁴ The use of this very neat method of straining material seems happily used in this instance. Professor Sauveur's revival of the torsion test fits in with the engineer's desire for a simple method of test and a simple piece of equipment, and in this case if the extrapolation that Mr. Brophy shows at the conclusion of his paper is checked and verified, we will certainly have a much nicer way of testing creep than our present methods.

I would like to say a few words in regard to stepped stress-strain curves because I happen to have worked on that in 1915. I was particularly interested in those days in why it was that steps had long been overlooked, and I think it is more or less apparent that our ordinary testing machines do not show them because we do not have constant rate of loading and we do not have freedom of elongation independent of the load; but with a dead weight testing machine, the steps are very much more apparent than under ordinary conditions, and they appear in many alloys.

With wire specimens 20 inches long and 0.030 inch diameter, steps or waves appeared in electrolytic copper, but they were more prominent in other materials. It seems probable that in general there is a condition of rate of loading and temperature at which steps appear in any given material. Above or below that temperature, which may be below atmospheric, the curves will be smooth.

²Leland Russell van Wert, "Some Notes on Blue Brittleness," American Institute of Mining and Metallurgical Engineers, Technical Publication No. 404, 1931.

³Albert Sauveur, "Steel at Elevated Temperatures," *TRANSACTIONS, American Society for Steel Treating*, Vol. XVII, No. 3, 1930.

⁴Research Engineer, American Chain Co., Bridgeport, Conn.

If it turns out that pure metals develop steps at any temperature, the precipitation theory will have to be refined a little to explain the phenomena.

R. S. ARCHER:⁶ There are two comments I would like to make. As to the method of testing, I think it is interesting to note the very good use that has been made of the torsion test by Mr. J. V. Emmons in the testing of hard tool steels. Mr. Emmons has a paper at this meeting on high speed steel.

In reference to the step diagrams, I believe comparable phenomena have been shown in some of the aluminum alloys, especially the age-hardening aluminum alloys.

Author's Closure

I wish to thank the gentlemen who have offered discussion of this paper. I wish to emphasize that all the material in this paper should be accepted with reservations since it is realized that the conclusions are perhaps radical. It is proper that further work by the author and others should be done before the ideas be accepted.

It is pleasing to see such confirmation of data by another investigator. The one discrepancy between Mr. Kanter's work and the author's is as to the influence of heat treatment. The differences may result from the fact that the author's stresses were much higher than Mr. Kanter's, so that the hardening due to precipitation (if any) under stress at elevated temperatures exceeded that obtained in Mr. Kanter's work, and was sufficient to overcome the tempering effect.

The material used for the tests shown in Fig. 7 was annealed.

In answer to Mr. Laverne's questions (a), (b), and (c), may I say that in all tests the shot was transferred in five-pound lots which were weighed to within one-half ounce. Each lot was then poured in slowly, the total loading period in the case of tests shown in Figs. 1, 2, and 3 being approximately eight to ten minutes.

The instantaneous deformation was read after each increment. When a step occurred the loading was stopped and the load noted; the step was allowed to go to completion before loading was resumed.

Regardless of the accuracy of the weighing, there is no difficulty in plotting the data. The loads were measured to within one-half ounce and the twist measured to one-tenth of a degree. This answers question (d).

In answer to question (e) the rates of loading were approximately constant in all tests. No particular effort was made in this direction, but a series of motions performed in routine tend to become uniform in duration.

I wish to apologize to Mr. DeForest for not having acknowledged his previous work. This was an oversight.

⁶A. O. Smith Research Corp., Milwaukee.

SOLUBILITY OF OXYGEN IN SOLID IRON

BY N. A. ZIEGLER

Abstract

The dissolving power of iron for oxygen at all temperatures up to 900 degrees Cent. (1650 degrees Fahr.) is very small (within the experimental error). At 700 degrees Cent. (1290 degrees Fahr.) it begins to increase slowly, at 900 degrees Cent. (1650 degrees Fahr.) rapidly, and reaches its maximum value of about 0.10 per cent in the neighborhood of 1000 degrees Cent. (1830 degrees Fahr.)

Presence of carbon in iron very considerably reduces its dissolving power for oxygen at all temperatures.

Preliminary curves, representing the equilibrium between iron, carbon and oxygen, in solid iron at different temperatures are presented.

THE influence of oxygen on the physical and mechanical properties of iron and its alloys is a problem of great importance both from practical and scientific points of view. This problem has been attracting attention of investigators in different countries for years, but work on it has been particularly active during the last decade.

In 1921 Stead (1)¹ and Whiteley (2) made attempts to determine the quantity of oxygen in steels by selective etching of a polished sample. In replying to a discussion of his paper, Dr. Stead made the statement that "there was so much assumption unaccompanied by solid scientific fact that it was essential that much more be done in the direction of determining what the limit of solubility actually was."

Soon after this challenge, several scientists set to work on this problem. Herty and his associates tackled it from the practical side, and in a series of excellent papers (3) secured international fame by giving to steel and foundry men valuable information for improving their products.

¹The numerals appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, N. A. Ziegler, is a member of the society. He is associated with the research laboratories of the Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. Manuscript received April 18, 1931.

Feild made an attempt to express the changes taking place during the preparation of iron alloys by means of mathematical equations (4). Based on his results, Kinzel and Egan (5) determined experimentally the numerical value of the FeO-C equilibrium constant* in an iron bath at a temperature of 1550 degrees Cent. (2820 degrees Fahr.) and at atmospheric pressure, and found this to be 5×10^{-4} . This value is considerably lower than reported by other investigators. (Herty (5) obtained 0.010–0.030, and Vacher and Hamilton (6) obtained 0.011).

Tritton and Hanson were the first to make an attempt to construct an iron-oxygen constitutional diagram, based on experimental evidence (7). Later this attempt was repeated by Benedicks and Lofquist (8), and still later by Oberhoffer (9).

Grossmann published a paper on "Oxygen Dissolved in Steel, and its Influence on the Structure" (10), and later, in 1930, delivered the Campbell Memorial Lecture on the same subject (11). In spite of the considerable amount of work done on this problem, however, he is perhaps justified in stating that "the question whether the oxygen is truly in the dissolved state is a theoretical matter awaiting further evidence."

Schenk and his co-workers (12) performed a series of experiments, saturating samples of iron with oxygen in an atmosphere of CO₂, or in a mixture of CO₂ and CO. They report that the maximum solubility of oxygen in iron at 800 and 1000 degrees Cent. (1470 and 1830 degrees Fahr.) is about 0.5 per cent and at 700 degrees Cent. (1290 degrees Fahr.) about 0.8 per cent. Krings and Kempkens (13) made an attempt to saturate iron with oxygen by heating samples in an atmosphere of hydrogen containing different amounts of steam. They report the maximum solubility of oxygen at 750 degrees Cent. (1380 degrees Fahr.) to be 0.11 per cent. These inconsistencies can only be explained by a catalytic action of some of the oxidizing gases and by a possibility of formation of oxides within the sample, in addition to oxygen absorbed as a solid solution.

The most difficult part of this problem was to develop a reliable method for analyzing oxygen in metals. This was solved satisfactorily by Oberhoffer and his colleagues, and the results published in a series of articles (14). Unfortunately, this work was left uncompleted, due to the death of this distinguished scientist.

* $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$
Per Cent FeO \times Per Cent C = equilibrium constant.

Quite independently, Jordan (15) developed a method for determining oxygen in alloys, similar to Oberhoffer's and differing from it only in detail. The principle of Oberhoffer's method is to melt a sample in vacuum in a graphite crucible, converting dissolved oxygen and oxides present into CO. The gases given off during this process are collected and analyzed by a volumetric method. Jordan's method is essentially the same, the only difference being that the gases are analyzed gravimetrically.

At the same time as Oberhoffer and Jordan were developing their methods for determination of oxygen in metals, the author, in cooperation with P. H. Brace, was working on the determination of gases given off by metals when melted in a vacuum. At that time little was known about the reactions between refractory oxides at high temperatures, in contact with carbon present in the iron bath. Based on certain experimental evidence, the conclusion was reached that some refractories, such as aluminum and zirconium oxides, are not reduced under the above conditions. (16) and (17). However, discussions of the published results and subsequent repetition of the experiments showed that the original results were not reliable. To obtain correct results a new type of vacuum high frequency furnace was designed and built. (Fig. 1). This furnace is constructed exclusively of silica, glass and vacuum cement, all metallic parts being eliminated. A sample is melted in a gas free graphite crucible, and degasified at about 1600 degrees Cent. (2910 degrees Fahr.). Products of this degasification are collected and analyzed by the volumetric method, previously described (16).

The chief objection to the graphite vacuum fusion method of oxygen determination is the uncertainty as to the behavior of different oxides under the above conditions. The opinions of different authorities on this subject differ. Jordan (15) and Thanheiser (18 and 19) are of the opinion that the reduction of all oxides which may be present in iron alloys, under the above conditions, is complete. There are others, however, who are doubtful that oxides of aluminum and magnesium can be completely reduced by graphite vacuum fusion.

The author placed known amounts of Fe_3O_4 , SiO_2 , and Al_2O_3 in small cups made from degasified and deoxidized high carbon iron, and analyzed for oxygen in the usual way. The results showed that in 15 minutes (length of time necessary for degasifying an average sample) Fe_2O_3 was reduced 100 per cent, SiO_2 —2.2 per cent and

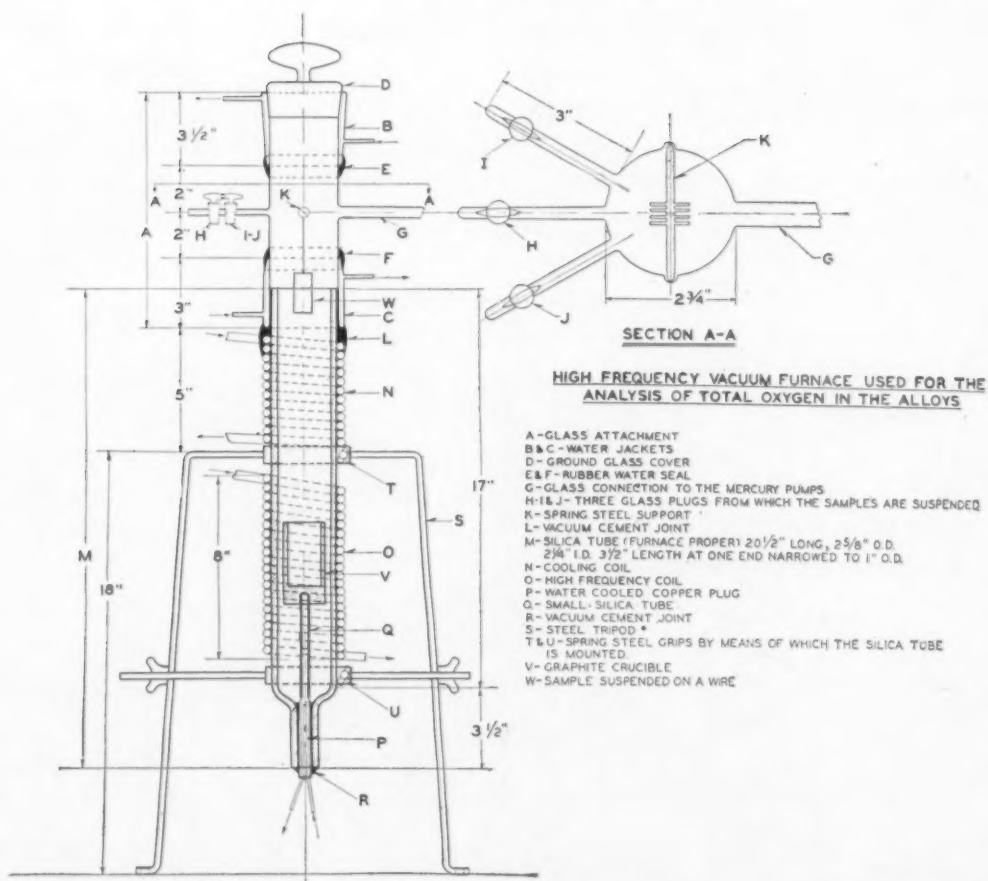


Fig. 1—High Frequency Vacuum Furnace Used for the Analysis of Total Oxygen in the Alloys.

Al_2O_3 —0.85 per cent. When, after the analyses, the resultant little ingots were examined, the silica and alumina were found on the surfaces of the charges. However, it must be assumed that silica and alumina, which may be present as inclusions in iron alloys, under similar conditions will not necessarily behave in the same way, and, therefore, the above experiment is not a proof that such inclusions are not reduced by the above method. The main difficulty of studying oxygen in iron alloys is that it may be present in a large variety of chemical compounds, widely differing one from the other in their chemical and physical properties. However, if experiments were restricted to alloys containing iron, carbon, and oxygen only, the problem is greatly simplified, because it is a well established fact that alloys of this type are completely reduced by the graphite vacuum fusion method.

This is the type of alloys used by Tritton and Hanson in their

investigation of solubility of oxygen in iron (7). They show definitely that for every temperature there is a certain limit to the amount of oxygen that can be in solution in iron. However, as they did not use vacuum melting for the preparation of their alloys, the minimum oxygen content of their samples was 0.08 per cent. At high temperatures, at which the solubility of oxygen in iron is about 0.21 per cent, these samples were satisfactory, but for the work at temperatures below 1000 degrees Cent. (1830 degrees Fahr.), they were of little value.

The author attacked this problem in a somewhat different way. Several ingots of iron were prepared in a bell jar vacuum furnace (16), and deoxidized by the addition of small amounts of carbon. From these ingots small samples were machined, the size, shape, and chemical composition of which are given in Table I. Each one of

Table I
Chemical Analysis of Several Ingots

Sample No.	Size (in inches)	C*	O ₂	S	P	Si	Mn
I- 46(A-R)	$\frac{3}{8} \times \frac{3}{8} \times 1\frac{1}{2}$.0095	.001				
I-116(A-L)	$2 \times 1 \times \frac{1}{8}$.0040	.016			Traces	
I-117(A-B)	$2 \times 1\frac{1}{2} \times 1\frac{1}{2}$.0024	.022				
I-118(A-K)	$2 \times 1 \times \frac{1}{8}$.0022	.009				
I- 45(A-L)	$\frac{1}{2} \text{Rd} \times 1$.0049	.082				

*All carbon determinations were performed by "Yensen" method. (20)

these samples was suspended from a nickel wire (at higher temperatures platinum wire was used) in a vertical silica tube furnace, closed at the top and open at the bottom (Fig. 2), and heated up to the desired temperature in a nitrogen atmosphere. When this temperature was reached, oxygen was substituted for nitrogen, and the sample kept in the oxygen for a certain period of time, after which the wire was cut, and the sample quenched in cold water. The following tabulation shows the periods of time for which different samples were kept in the oxygen atmosphere:

I- 45(A-L)	1 hour
I- 46(A-R)	1 hour
I-116(A-L)	$\frac{1}{2}$ hour
I-118(A-K)	$\frac{1}{2}$ hour
I-117(A-B)	2 hours

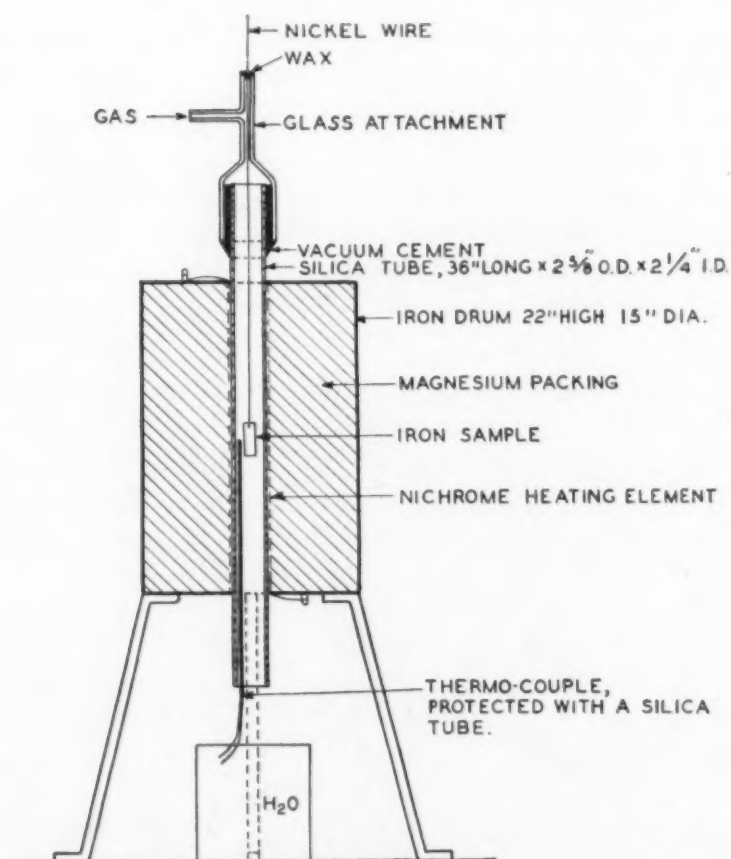


Fig. 2—Electric Furnace Used for Treating Samples in Oxygen Atmosphere and Subsequent Quenching in Water.

Specimens I-116J and K, which were treated at 1200 degrees Cent. (2190 degrees Fahr.) were kept in the oxygen atmosphere for 5 and 6 minutes respectively, because at this temperature oxidation of iron is so rapid that a longer period would cause complete oxidation.

This procedure was based on the assumption that if iron has a certain dissolving power for oxygen at a given temperature, the sample should become saturated with the oxygen, and on drastic cooling retain it either as super-saturated solid solution, or as precipitated iron oxide. The scale formed on the surface of the samples was removed by grinding and etching in alcoholic HCl, and the cleaned samples were then analyzed for oxygen. The results of these analyses have been plotted against the temperatures at which the samples were quenched. (Fig. 3.) It is apparent that up to 700 degrees Cent. (1290 degrees Fahr.) dissolving power of iron for oxygen is negligibly small (within experimental error), at 700 degrees Cent. the

solubility begins to increase slowly, at 900 degrees Cent. (1650 degrees Fahr.) rapidly and reaches its maximum value of about 0.10 per cent in the neighborhood of 1000 degrees Cent. (1830 degrees Fahr.).

The question was raised, whether or not an iron sample, $\frac{1}{8}$ inch thick, can become saturated with oxygen in one-half of an hour. For this reason two larger samples, I-117 (A&B) $2 \times 1\frac{1}{2} \times 1\frac{1}{2}$ inches, were treated in a similar way, i.e., heated in an oxygen atmosphere for two hours, one at 900 degrees Cent. (1650 degrees Fahr.); the other at 1000 degrees Cent. (1830 degrees Fahr.) and quenched in water. After removing the surface scale, both samples were cut into thin plates, and each cut was analyzed for oxygen separately, thus showing to what extent the oxygen had penetrated the sample. The results are given in Table II.

Table II
Oxygen Penetration

Sample No.	Quenched from Degrees Cent.	Original Carbon Content Per Cent	Oxygen Per Cent			
			Original	First Cut	Second Cut	Third Cut (center)
I-117A	900	0.0024	0.022	0.045	0.047	0.044
I-117B	1000	0.0024	0.022	0.085	0.086	0.079

It is evident from Table II that the distribution of oxygen in a sample with less than 0.01 per cent carbon is fairly uniform, and that, since a 2-hour period is sufficient to saturate homogeneously a sample $1\frac{1}{2}$ inch thick, $\frac{1}{2}$ hour should be ample time in which to saturate a sample $\frac{1}{8}$ inch thick. It may be mentioned, that the average oxygen content of a $\frac{3}{4}$ -inch round bar, forged at about 1000 degrees Cent. (1830 degrees Fahr.) from an oxygen free ingot, is found to be 0.09 per cent, which agrees very well with the saturation value at that temperature (0.10 per cent).

Some commercial steels were analyzed, and the results are given in Table III. The average oxygen content of Armco iron recorded in Table III is 0.086 per cent, which again is in good agreement with the saturation value of iron at 1000 degrees Cent. (1830 degrees Fahr.).

No attempts were made to determine the allotropic transformation points in iron-oxygen alloys by any direct method. The appear-

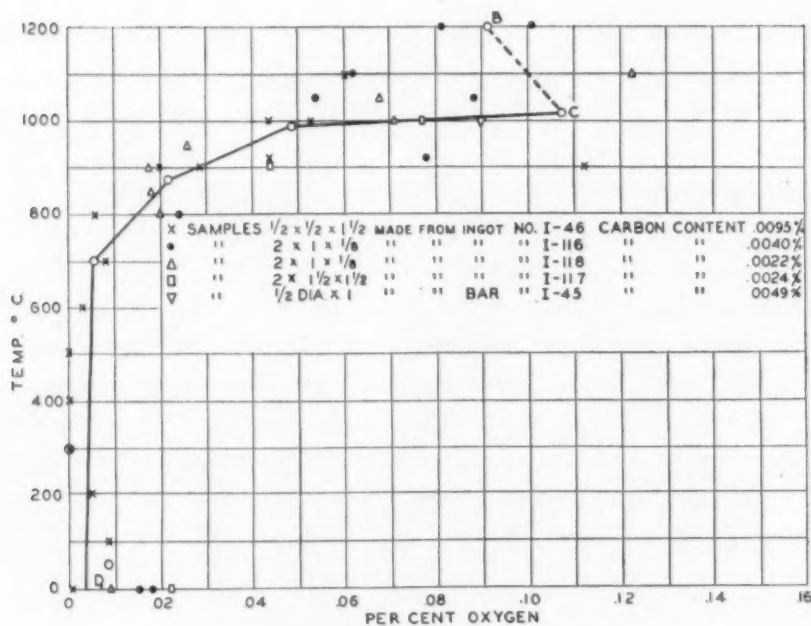


Fig. 3—Solubility of Oxygen in Solid Iron.

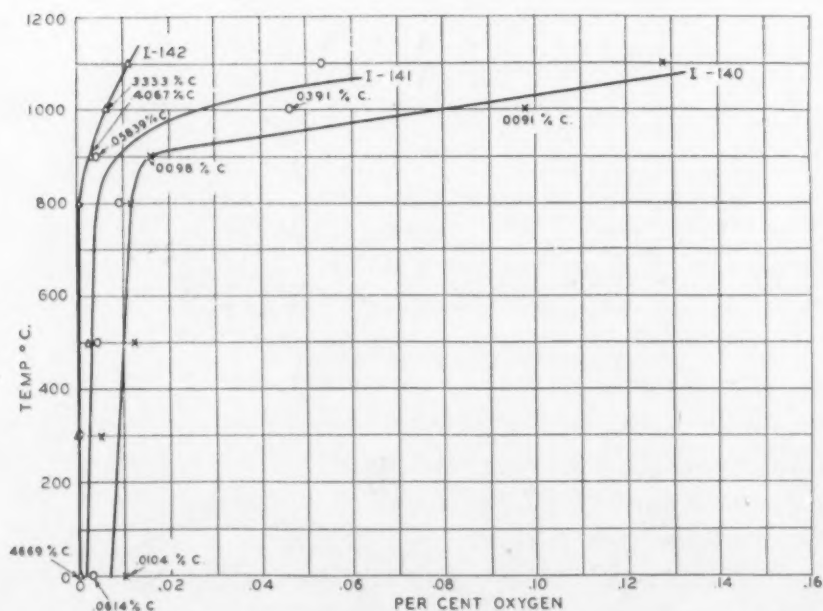


Fig. 4—Effect of Carbon Present in the Sample on its Saturation Value for Oxygen.

ance of the curve in Fig. 3 suggests a "peritectoid" reaction (increase in solubility at temperatures higher than 900 degrees Cent.). Tritton and Hanson (7), however, report that in samples saturated with

Table III
Chemical Analysis of Several Commercial Steels

	C	S	P	Mn	Si	H ₂	N ₂	O ₂	Cr	Mo
	Open	Hearth	Product							
Spoon test poured into a small mold	.15	.035	.015	.16001	.001	.030		
Spoon test poured into a small mold	.20	.035	.016	.45	...	trace028		
Spoon test poured into a small mold	.22	.036	.015	.40026		
Spoon test poured into a small mold	.19	.045	.016	.40	trace	.018		
Spoon test poured into a small mold	.34	.033	.016	.66	.15002	.014		
Ingot material	.18	trace035		
Ingot material	.25017		
Ingot material	.20	trace020		
Ingot material	.21030		
Armco Iron	.016113		
Armco Iron	.008091		
Armco Iron	.012080		
Armco Iron110		
Armco Iron080		
Armco Iron with 70 ft.-lbs. impact value001	.021	.057		
Armco Iron with 3 ft.-lbs. impact value004	.084		
Miscellaneous Samples										
Electric Steel Forging	1.0030015	1.8	1.8
Electrically welded joint093	.183		
Electrically welded joint127	.259		
Oxyacetylene-welded joint	High impact values				005	.017	.053	
Atomic hydrogen welded joint					013	.054	

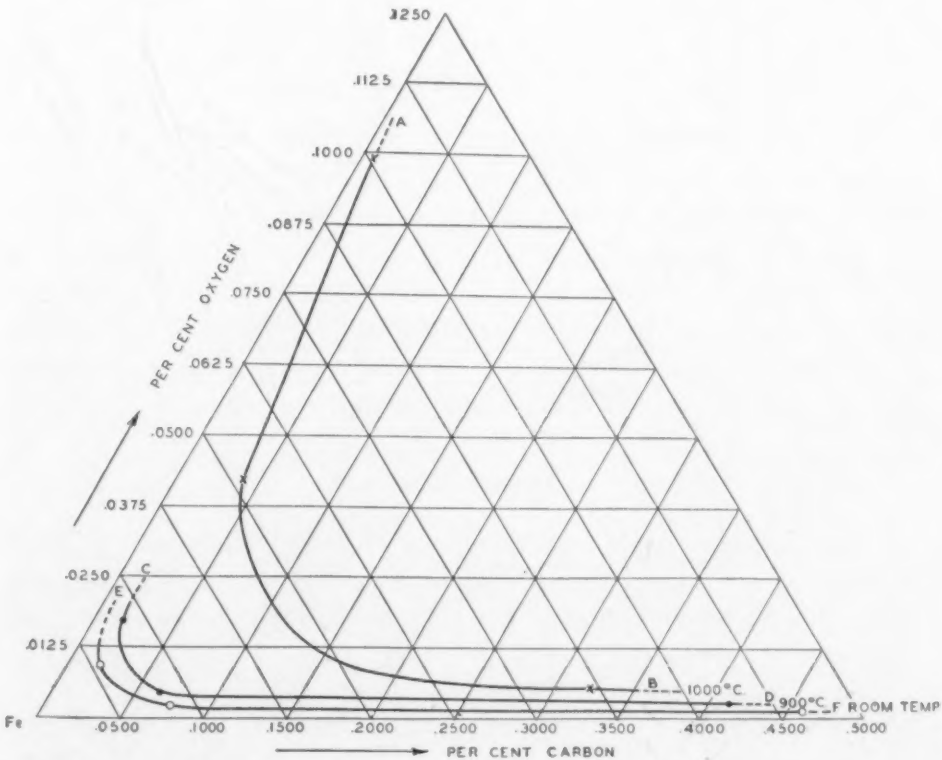


Fig. 5—Limits of Solubility of Oxygen in Iron-Carbon Alloys at Different Temperatures.

oxygen (0.1 — 0.21 per cent O_2), the A_3 point is found at 845-861 degrees Cent. (1553-1582 degrees Fahr.), which indicates a eutectoid reaction. Hence, to solve this question further experimental data are necessary.

All samples investigated so far were low in carbon (less than 0.01 per cent). Three additional samples with 0.0104, 0.0614, and 0.4669 carbon respectively were selected, machined into $\frac{1}{8}$ -inch plates, treated, and analyzed for oxygen in the way previously described. The results obtained are shown in Fig. 4. Some of these oxygen-treated samples were also analyzed for carbon (Fig. 4), so that from this data the approximate equilibrium conditions for iron-oxygen-carbon, i.e., maximum solubility of oxygen in iron alloys with different amounts of carbon, can be plotted in the form of a ternary diagram. (Fig. 5).

Curve AB represents maximum solubility of oxygen in iron-carbon alloys at 1000 degrees Cent. (1830 degrees Fahr.), CD at 900 degrees Cent. (1650 degrees Fahr.) and EF at room temperature. However, results represented in Figs. 4 and 5 should be regarded as qualitative, rather than quantitative.

SUMMARY

1. The solubility of oxygen in iron (with less than 0.01 per cent carbon) at temperatures up to 800 degrees Cent. (1470 degrees Fahr.) is negligibly small (within experimental error).
2. The solubility increases rapidly above 900 degrees Cent. (1650 degrees Fahr.) and reaches a maximum of about 0.10 per cent in the neighborhood of 1000 degrees Cent. (1830 degrees Fahr.)
3. The presence of carbon reduces very considerably the saturation value of iron for oxygen at all temperatures.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Dr. T. D. Yensen, for his cooperation in interpreting the results and preparing the manuscript and to Mr. Wilson Scott for his help in the experimental part of the work.

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DISCUSSION

Written Discussion: By Yap, Chu-Phay, physical metallurgist and chemist, 27 Grove St., New York City.

This paper represents such a beautiful piece of experimental work that I am sure it will stand as a classic example for us to emulate. It has everything that characterizes a great piece of work: style, elegance and thoroughness. I have spent many hours reading and re-reading this paper, in order fully to grasp the tremendous experimental difficulties that Mr. Ziegler has been able to overcome, which he so modestly understates. I would like to offer a few comments which I hope might be of some interest to Mr. Ziegler and my colleagues.

I. This paper raises the question again as to whether oxygen is dissolved in solid iron as a gas or as compound (FeO). If oxygen exists as a gas, is it in the ionic, monatomic or molecular state? The phase rule and certain free energy considerations can, it seems to me, throw considerable light on the problem. Fig. 1 of this discussion shows the *ideal* solubility curve of a gas in a solid metal with a transition point at T. On account of the small solubilities, we shall find the curve A-B and C-D to be linear. If the gas were diatomic

and suffers dissociation when dissociation is in the gamma form, then the solubility curve above the transition temperature will slope downward, as shown by C-D'.

On the other hand, if the dissolved gas forms a compound with the solvent metal¹ then the path of solubility curve will be that shown by M-N-F, with a sharp intersection (N) at the transition temperature, which constitutes an invariant triple point. This is in accord with the deductions of the phase rule.

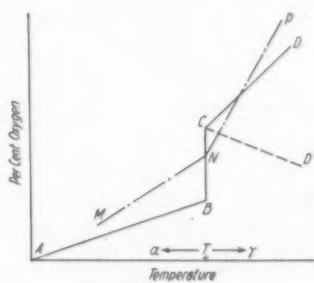


Fig. 1

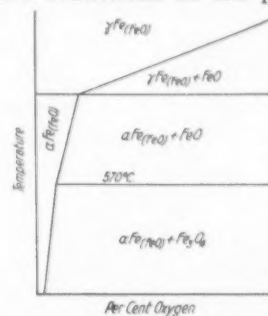


Fig. 2

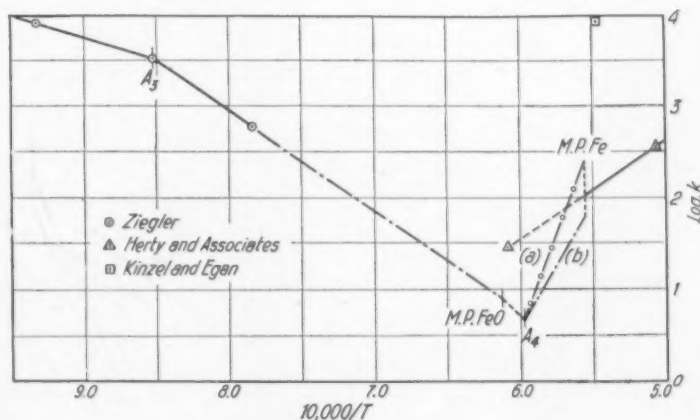


Fig. 3

Except for the fact that the two branches of the curves (M-N and N-P) in Fig. 4 of Mr. Ziegler's paper do not intersect sharply, his solubility curves indicate the formation of FeO, so that the term "solubility" of oxygen is slightly misleading. (Incidentally, the term "occlusion" is even worse.)

On the basis of free energy considerations, if the molal free energy of formation of the compound is negative, that is, the compound is stable, the partial molal free energy of formation of the compound in solid solution must be equal to the former, because the solid solution is in equilibrium with the solid solute (compound). Moreover, since we are not dealing with polar compounds, our problem is thus considerably simplified: we merely calculate the free energy of formation of the compound, which in turn would enable us at once to calculate its partial molal free energy in the solid solution at any concentration.

¹The method of measuring the electrode potential should give clear evidence as to whether or not the gas forms a compound with the solvent metal. Consult, for example, Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," New York, 1923. McGraw-Hill Book Co.

For this purpose, we need but consider its activity equal to the concentration.

II. As FeO becomes unstable below 570 degrees Cent. (1060 degrees Fahr.), undergoing a transformation to magnetite, we have another triple point at that temperature, as shown in Fig. 2 of this discussion. Since the transition only takes place in crystalline FeO, the FeO in solid solution in alpha iron is, therefore, unaffected, although as the temperature decreases below 570 degrees Cent. (1060 degrees Fahr.) the excess FeO which is precipitated will change to Fe₃O₄.

III. Two years ago, in discussing a paper by Dr. Yensen² on the probable absence of allotropy in absolutely pure iron, I called attention to the fact that from thermodynamic considerations we may expect the A₃ point to be raised as the iron approaches extreme purity. A close study of Fig. 3 (Figs. 4 and 5 being merely its derivative) does suggest the possibility that A₃ may be located at 1000 degrees Cent. (1830 degrees Fahr.). There are, of course, two simple alternative explanations: (1) According to Smits' theory of allotropy, we should expect that in very pure metals, the allotropic change takes place very slowly, as reversible transitions are known to be autocatalytic; (2) There is some doubt in my mind as to whether or not equilibrium has been truly established, not so much with respect to the gas, but much more with respect to the metal phase. I am not at all certain that even after half an hour, the alpha form completely changes over to the gamma form. In this kind of work, one cannot take anything for granted.

IV. One may consider the equilibrium involving γ Fe, FeO and Fe₃C according to the following equation:



Since free energy equations can be added and subtracted like thermochemical equations, let us consider the following:



Subtracting equations (2) and (3) from (4) gives equation (1), so that

$$\Delta F_1 = \Delta F_4 - \Delta F_2 - \Delta F_3 \quad (5)$$

I have already given elsewhere³ free energy equation (2) which I have good reasons to believe is more accurate than the others previously given (e.g., by Eastman and by Ralston) in the range of 900 to 1360 degrees Cent. (1650 to 2480 degrees Fahr.), referring to gamma iron as the standard state above the A₃ point up to the A₄ point. As I have already obtained values of ΔF_3

²Transactions, Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, 1929, p. 320.

³Discussion of paper on "Scaling of Steel at Elevated Temperatures, Etc.," by Messrs. Murphy, Wood and Jominy, TRANSACTIONS, American Society for Steel Treating, Vol. 19, No. 3, January 1932, p. 193.

between 750 and 1100 degrees Cent. (1380 and 2010 degrees Fahr.), which I am convinced are quite accurate, then it is comparatively simple to calculate ΔF_1 , free energy equation (4) being already known over a large range of temperature. It is not my intention, however, to calculate ΔF_1 at this time, because I do not wish to detract any interest away from the paper under discussion.

V. Herty and co-workers⁴ have done an exceptional piece of work in their study of the equilibria of iron, oxygen and carbon in the liquid state. On the reasonable assumption that the activity of molten iron and of the CO (1 atmosphere) is unity, then the equilibrium is

$$\begin{aligned} k &= [\text{CO}](\text{Fe})/(\text{C})[\text{O}_2] \\ &= 1/(\text{C})[\text{O}_2] \end{aligned} \quad (6)$$

Assuming that the heat of reaction is constant over a short range, then if we plot $\log k$ against $1/T$ we should obtain a straight line. In Fig. 3 I have reproduced Herty's curve as shown. In order to show in a qualitative way the change in the equilibrium with respect to temperature and change of phase, I have calculated the corresponding values of k from Mr. Ziegler's data for 800, 900 and 1000 degrees Cent. (1470, 1650 and 1830 degrees Fahr.) as shown in Fig. 3. Assuming again the heat of reaction is constant, we can then extrapolate the curve to 1360 degrees Cent. (2480 degrees Fahr.), the melting point of FeO, another triple point. From free energy considerations, we know the $\log k \cdot T^{-1}$ should curve downward more in the range in which liquid FeO is in equilibrium with delta iron. Between the A_4 and the melting point of iron, I have drawn two curves, (a) and (b). As the melting point of FeO is below that of iron, I, therefore, treat the equilibrium at the melting point as mono-variant rather than as invariant (triple point). From Mr. Ziegler's own work in collaboration with Mr. Brace,⁵ they observed an increase in pressure just below the solidification point of iron and, consequently, it is only reasonable to infer that curve (a) is more probably the correct one. However, whether (a) or (b) is correct, we know at least that the solubility of FeO in delta iron is much less than in gamma iron.

VI. In Fig. 3 of Mr. Ziegler's paper, we note that B-C suggests a retrograde solubility. This seems to me to be an error, as a rough calculation of ΔF_{1-1470} does not show this. It is noteworthy that Mr. Ziegler, in order to avoid excessive oxidation of his samples, soaked them for only 5 to 6 minutes at 1200 degrees Cent. (2190 degrees Fahr.). Equilibrium could hardly have been established in such a short time, in spite of the high temperature. He could have avoided too rapid oxidation of his samples by diluting his oxygen gas with, say argon, so that the partial pressure of oxygen may be kept down fairly low—keeping, of course, the total pressure at one atmosphere.

VII. The value of m (the product of FeO \times C) at 900 and 1000 degrees Cent. (1650 and 1830 degrees Fahr.) are respectively 0.00133 and 0.00755. On

⁴Bulletin No. 34, Mining and Metallurgical Investigations, Carnegie Institute of Technology, Pittsburgh, 1927.

⁵Technical Publication No. 59, American Institute of Mining and Metallurgical Engineers, 1928.

the basis of these values, the isothermal solubility curves for these two temperatures, shown in Fig. 5, may be redrawn as hyperbolic curves on rectangular coordinates, for purposes of interpolation.

Written Discussion: By Dr. Ing. Werner Hessenbruch, Birkenhainerstr. 35, Hanau, A. M. Germany.

I beg Mr. Ziegler to receive my best congratulations for his paper. He has worked on one of the most important questions of iron metallurgy, the solubility of oxygen in solid iron. It is a pity I cannot personally answer on the most interesting observations Mr. Ziegler has made.

It was of great interest to note, that Mr. Ziegler has used the method of determination of gases, which P. Oberhoffer and collaborators on the continent as well as L. Jordan and I. R. Eckman in the States have developed. The experiments in respect to the reduction of pure oxides could not succeed, just as our own preliminary experiments in this line did not succeed because we made the same mistakes as did Mr. Ziegler. It can be shown, that the moment you throw a small piece of oxide on the surface of the molten iron bath a spontaneous evolution of gases occurs and small parts or a great deal of the oxides is thrown out of the graphite crucible. Dr. Diergarten⁶ has shown, that the complete reduction of SiO_2 , Cr_2O_3 and Al_2O_3 with the vacuum fusion method is possible. He used small boxes of iron, which were filled with the oxide and brought the oxides in nearer contact with the molten iron, saturated with carbon.

Concerning the mean experiments, the saturation of samples with oxygen, it would be of great interest to know, if Mr. Ziegler had checked his oxygen determinations by observations of the microstructure. The conclusions drawn are only correct if there have not been formed free oxides. It is well known, that if the solid solution is saturated the excess of oxygen is precipitated as oxides. If you anneal an iron sample in an oxidizing atmosphere for a fairly long time to a temperature of about 1000 degrees Cent. (1830 degrees Fahr.) you may observe under the microscope a continuous transition from the scale on the rim to the pure, unoxidized iron in the core. There is also a zone where the solid solubility is exceeded and free oxides are formed. Naturally a sample takes up more oxygen by annealing in an oxygen atmosphere if the temperature is higher. But it seems to me that it is not certain that the amount of oxygen does not exceed the solubility in the solid state.

In the summer of 1929 Dr. L. Treimen in the Eisenhütten-Institut der Technischen Hochschule at Aachen made similar experiments with a quenching apparatus. He annealed a sample of known oxygen content in a vertical silica tube in vacuum. The temperature was measured by a thermocouple near the specimen. After an annealing of about one hour the fine iron wire on which the sample was hanging was cut by a fairly high voltage and the sample dropped in the bottom end of the silica tube, filled with mercury. The mercury, extremely good, was cooled by a mixture of solid carbon dioxide and acetone on the outside of the silica tube. All samples were examined under the microscope before and after vacuum annealing. Treimen says in his report⁷

⁶Archiv für das Eisenhüttenwesen, Vol. 3, 1929-30, p. 577 to 586.

⁷Dr. Ing. Dissertation, Aachen 1929, unpublished.

that he could observe that the small precipitated oxides by annealing and quenching went in solution. But the diffusion of oxygen was extremely low. Around the greater inclusions small rings were formed which seemed to be the solid solution of oxygen in iron. In no case did the larger oxides go completely into solution. These experiments show how difficult it is to estimate the solubility of oxygen in solid iron.

Written Discussion: By Ralph W. E. Leiter, research metallurgist, Edward G. Budd Mfg. Co., Philadelphia.

Mr. Ziegler concludes that the solubility of oxygen in iron (with less than 0.01 per cent carbon) is negligibly small at temperatures up to 800 degrees Cent. (1470 degrees Fahr.).

It seems to me that the data obtained is not complete enough for the above conclusion. If I understand correctly, the samples of iron were placed in oxygen only one-half hour at even the lowest temperature investigated. Mr. Ziegler shows by experiment that samples of iron held one-half hour at 900 and 1000 degrees Cent. (1650 and 1830 degrees Fahr.) are saturated with oxygen. I should like to see the same experiment made at say 500 and 700 degrees Cent. (930 and 1290 degrees Fahr.) and would expect that considerably longer time would be required to saturate the specimens with oxygen at these lower temperatures. In other words it seems quite probable that the oxygen (or oxide) diffusion rate in solid iron would decrease with decreasing temperature. If such is the case the solubility of oxygen in iron, as found by Mr. Ziegler, may be low at temperatures of 800 degrees Cent. (1470 degrees Fahr.) and below.

Written Discussion: By Dr. R. Wasmuht, engineer, Fried. Krupp, Aktiengesellschaft, Essen, Germany.

The paper of Ziegler is a very welcome contribution to the problem of the solubility of oxygen in solid iron. It recommends itself by the simple and clear way of the method and arrangement of the investigations. It is a novel fact that the saturation of the samples with oxygen was completed in such relatively short space of time as half an hour or 2 hours respectively, whereas other investigators, e.g., Krings and Kempkens or Schenk, required considerably longer periods for this saturation, using, however, other gaseous phases. The order of magnitude of the saturation limit found is in agreement with the values to be expected according to the results of the most recent researches. It is true that in most cases the maximum solubility is assumed to occur at somewhat lower temperatures. On the other hand, as the author rightfully indicates, the values obtained at higher carbon contents seem to be of a merely qualitative character. Evidently a reaction of the carbon content with the oxygen present took place, as the samples showed a constant decrease of carbon content with increasing oxygen absorption, as illustrated by Fig. 4. Ziegler's findings evidently only apply to pure Fe-O or Fe-FeO alloys respectively. In practice we shall always have to reckon with additional alloying elements, such as manganese, silicon, etc., which will to some extent affect the solving power of the iron for oxygen. Besides, the form in which the oxygen gets into the iron will not be irrelevant. In Ziegler's present experiments oxygen is obviously brought into contact with the iron in the form of FeO and is also dissolved in it as FeO. It would be much appreciated

if the author would also investigate the problems pointed out, using for the purpose his quick and accurate working method, with the aid of the determination of oxygen as residue, finding in this way not the total oxygen content itself but its different combinations.

Written Discussion: By Robert F. Mehl, assistant director, research laboratories, The American Rolling Mill Company, Middletown, Ohio.

The determination of the solubility of oxygen in solid iron, as Mr. Ziegler points out, is of considerable technological importance. The determination of this solubility, and that of carbon, nitrogen, and sulphur, in solid iron, bears the same importance in iron alloys as similar determinations in aluminum and other age-hardening alloys, for it becomes increasingly clear that these solubilities are intimately related to the behavior of technical iron and steel. Indeed, it is remarkable that attention to this type of problem has been given only in the last few years, though the importance of such attention has long been evident. It is especially pleasant, therefore, to welcome Mr. Ziegler's valuable contribution.

Previous to Mr. Ziegler's work, the most satisfying contribution to the subject was that of Krings and Kempkens, to which Mr. Ziegler refers. Since their work was performed in a radically different way, and produced radically different results, it might be well to itemize the details of their technique. Krings and Kempkens made use of the physico-chemical principle that in the absence of solid solutions a solid will not react with a gas until the dissociation pressure of the first compound between the solid and the gaseous element is attained in the gas phase, but when solid solutions are formed, the solid will begin to react with the gas at negligibly low pressures, absorbing more and more gas as the pressure in the gas phase is increased, until the dissociation pressure of the compound is reached, beyond which the solid absorbs gas at a constant pressure until it is entirely converted into the compound; thus, at pressures below the dissociation pressure the solid will take up a definite amount of gas along a definite equilibrium curve. Krings and Kempkens determined this curve for powdered iron in a mixture of hydrogen and water vapor and found the composition of the iron to be 0.11 per cent oxygen at 715 degrees Cent. (1320 degrees Fahr.) when the partial pressure of the oxygen in the gas phase reached that of FeO , at which the iron is saturated with oxygen. But further than this, Krings and Kempkens approached the curve from each side, starting with iron in one case, and iron oxide in the other. Their curve thus represents a true equilibrium curve.

This solubility is far greater than Mr. Ziegler finds for a similar temperature. If Mr. Ziegler's solubility figures are low at temperatures below 900 degrees Cent. (1650 degrees Fahr.) it is probably because the time of exposure at these temperatures was insufficient to attain equilibrium. His data in Table II for temperatures of 900 and 1000 degrees Cent. (1650 and 1830 degrees Fahr.) are convincing enough concerning the attainment of equilibrium, but it is likely that at lower temperatures his figures are too low. As a matter of fact, at 900 and 1000 degrees Cent. (1650 and 1830 degrees Fahr.), his data (allowing for scattering) are not greatly different from those of Krings and Kempkens. At lower temperatures, however, the rate of diffusion of oxy-

gen in iron is very likely far less than at 900 degrees Cent. (1650 degrees Fahr.), for it is known that a hundred degree difference in temperature in some systems will alter the rate of diffusion by orders of magnitude. It appears, therefore, that some demonstration of saturation at temperatures below 900 degrees Cent. (1650 degrees Fahr.) is desirable, particularly since the data of Krings and Kempkens were attained under demonstrated equilibrium conditions. Such a demonstration would be particularly useful in a comparison of these two radically different methods.

It might be pointed out that the oxygen content of Armco ingot iron is not determined by a saturation of the solid iron with oxygen during processing; it is determined directly by the oxygen content of the liquid iron and the segregation process during freezing. The skin of the ingot contains much less oxygen than 0.086 per cent, the amount of oxygen increasing from the skin to the pipe. Finished sheets from the skin of the ingot have analyzed 0.030 per cent oxygen.

Written Discussion: By C. H. Herty, Jr., director of research, Mining and Metallurgical Advisory Board, Carnegie Institute of Technology, Pittsburgh.

This paper is a very interesting and thought-provoking one, and it would be most important that this research be carried out further in higher carbon ranges. On the three high carbon steels given, the oxygen content has dropped very sharply, but before curves as given in Fig. 4 can be quantitative it will be, of course, necessary to do much more experimental work at higher carbon contents.

It would appear that the author's method of studying oxygen absorption would be suitable for the determination of the rate of diffusion of oxygen—a point of great importance in determining the oxidation of a given steel at a given temperature in a given time. It would be interesting to know whether the original ingot structure would have any effect on the rate of oxygen diffusion. According to Grossmann's Campbell lecture last year, manganese prevented oxygen absorption during carburizing and it would seem that an opportunity to check this result is afforded in work of the type given in the present paper. It would also be interesting to know whether the high carbon steel was decarburized by this treatment.

Finally, would it not have been simpler to present Fig. 5 on a graph using only two coordinates rather than on a ternary diagram? After all, this is not a true ternary diagram; it is simply a different method of plotting the results, and to the reader who is not familiar with ternary diagrams this might be somewhat confusing.

Written Discussion: By Marcus A. Grossmann, associated with Illinois Steel Co., Chicago.

Mr. Ziegler has attacked an extremely important problem and has brought us some most interesting results. His saturation value, 0.10 per cent oxygen at 1000 degrees Cent. (1830 degrees Fahr.), agrees quite well with the results of a recent research at the University of Aachen.

Quite surprising, however, is the very high rate of diffusion indicating penetration through a $1\frac{1}{2}$ inch block in two hours at 1000 degrees Cent. (1830

degrees Fahr.), that is, at least $\frac{3}{4}$ inch from each side in two hours. In order to determine whether the same high rate of diffusion was found in ordinary vacuum-remelted open-hearth iron, tests were made on $\frac{1}{2}$ inch round cylinders $2\frac{1}{2}$ inches high. These contained about 0.01 per cent carbon, 0.01 per cent manganese and 0.021 per cent oxygen as vacuum-melted. Cylinders as described were heated at temperatures ranging from 1200 to 1800 degrees Fahr. for periods up to four hours at the lower temperatures and up to two hours at the higher temperatures. There was no appreciable increase in oxygen content, the original untreated samples varying from 0.017 to 0.022 per cent, while those treated at 1800 degrees Fahr. varied from 0.017 to 0.025 per cent. All oxygen determinations were made by the standard vacuum fusion method.

It will be interesting to pursue the subject further and discover the reason for the discrepancies in rates of diffusion.

Written Discussion: By T. D. Yensen, research laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh.

In regard to the question whether oxygen is dissolved in solid iron as a gas or as a compound (FeO) it seems a paradox.

Is it not clear according to our definitions and present conceptions that if a compound (FeO) is formed, it is precipitated from the solid solution and can be identified under a sufficiently powerful microscope as a separate phase? It may consist only of one iron atom and one oxygen atom, in which case we may call it a molecule of FeO, or it may consist of millions of each atom, but fundamentally the two cases are the same. In the first case, however, we shall not be able to see the particle even with our present most powerful microscopes and on this account are misled into the opinion that the impurity, in this case oxygen, is in solution in the iron, whereas it is obvious that this may not be the case. A more appropriate description would be "in solution or as colloidal precipitation" as distinguished from precipitated particles large enough to be seen under the microscope. The latter must contain at least a million atoms to be "seen" at a magnification of 5000 diameters. A gas molecule or globule such as O_2 would in this respect be a colloidal precipitate or a precipitated particle just as FeO or Fe_3C or FeS, etc., and a true solution would be possible only in case the impurity exists as atoms, either interstitial or substitution atoms.

Mr. Ziegler in his experiments did not, of course, depend upon microanalysis for his results. He started with very pure iron, heated it in oxygen to various temperatures, whereby oxides were formed on the surface from which oxygen atoms diffused into the interior, the amount of oxygen so diffusing into the iron depending on the solubility at the temperature in question. In quenching to room temperature some or much of this dissolved oxygen may be precipitated at the spot where it is located at the time of quenching, but will obviously remain in the sample, as a particle of precipitate cannot diffuse. After removing the outer layer of scale and determining the oxygen in the rest of the sample, the result will then give the total oxygen dissolved at the temperature to which it was heated.

The only question about the result is whether the samples were held at the various temperatures below 900 degrees Cent. (1650 degrees Fahr.) long

enough for the oxygen concentration to reach equilibrium, and this point may require further investigation.

Oral Discussion

G. R. FITTERER:¹ The author's results (given at the bottom of page 75) concerning the reduction of Fe_2O_3 , SiO_2 and Al_2O_3 by the vacuum fusion method are both interesting and important. It would, of course, be worth while to know the particle size of these various oxides and I would like to ask the author if he attempted to screen the particles to a given size which would be comparable to the dimensions of inclusions in steel. It is very likely that a slight decrease in the average particle size would give quite different results because the area of the oxide exposed would determine the rate of reduction.

The results listed in Tables I and II would be highly convincing if it were not for one vital point. Table II shows beyond question that the oxygen penetration at 900 to 1000 degrees Cent. (1650 to 1830 degrees Fahr.) was complete even in the case of abnormally large samples. However, it must be remembered that the rate of absorption of oxygen by gamma iron is much greater than would be the case for alpha iron. In other words, absorption of oxygen may have been complete in samples which were run above the A_2 point and yet have been incomplete below that temperature.

Hence I would like to ask Mr. Ziegler if samples similar to those listed in Table II were run at low temperatures. Confirmation of this point would necessarily have to be made at all temperatures before the solubility values listed in Table I and plotted in Fig. 3 could be made acceptable.

If oxygen absorption was not complete in the lower temperature samples the true curve which should be substituted for Fig. 3 will be shifted to the right, particularly in the low temperature ranges.

I do not wish to convey the idea that Mr. Ziegler's low temperature values are incorrect. On the contrary they may be absolutely correct, but tests should be made at temperatures lower than 900 degrees Cent. before their accuracy can be confirmed.

The author is unquestionably on the right track and has gone a long way toward solving the problem of solid solubility of oxygen in iron.

S. L. HOYT:² First of all I should like to associate myself with those who have expressed appreciation and commendation of this work by Mr. Ziegler, but I arise particularly to call attention to a point that seems to me worth while keeping in mind, and that is the distinction between methods of preparing alloys for study and the subsequent study of the equilibria in the system of iron and oxygen. The system itself is so unique that ordinary methods of preparation can hardly be employed. Possibly the paper may be construed as having dealt almost entirely with the first part of the program, i.e., the preparation of the alloys, and in that connection I should like to call attention particularly to a method that was used by Dr. Dushman and Mrs. Mary Andrews in their study of the tungsten-carbon system. Applying that method to this particular investigation would consist in using the same starting material

¹Associate metallurgist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

²Research Laboratories, A. O. Smith Corp., Milwaukee.

in the form of a wire and allowing it to absorb oxygen from an atmosphere which contains a rather low oxygen pressure and following some such property, for instance, as the electrical resistance, the better to be able to establish the moment when equilibrium has been attained.

I believe that in preparing alloys upon which a constitutional diagram is to be based, this consideration of equilibrium is extremely important. Dr. Herty points out the desirability of following rates. Incidentally, they could be followed by using the experimental procedure that I suggest.

As to the study of the constitution of the alloys, once having them prepared, I believe it would be worth while for Mr. Ziegler to examine his alloys by other means than simply analyzing them chemically. If that procedure were to be used for other alloys, I am sure that the evidence would be considered incomplete, and while comments of this kind may appear out of place to the experimenter who has had to solve so many real difficulties, to arrive at the point where he now is, I think that, nevertheless, they are justified to encourage him in this way to continue his work, and in that way to arrive at a better establishment of the iron-oxygen equilibrium diagram.

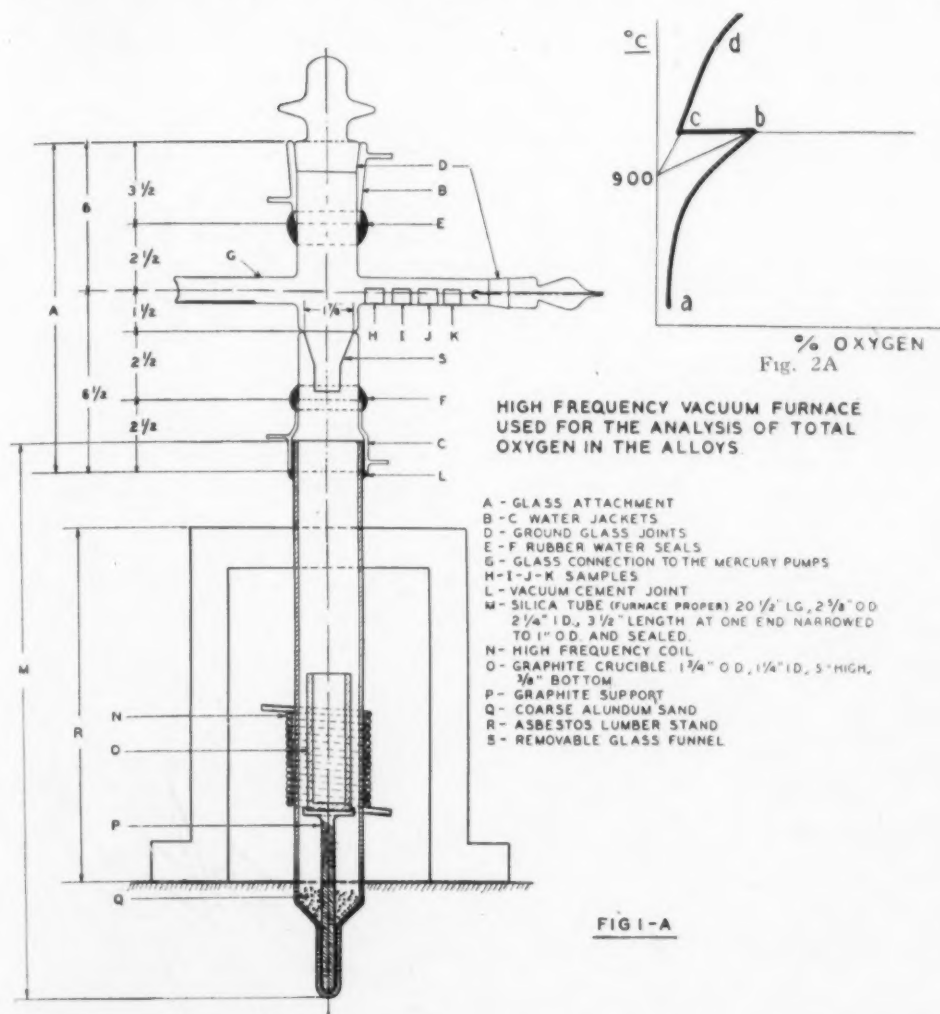
I cannot help thinking of the splendid discussion which we have heard from Mr. Yap on this paper, but at the same time if Mr. Yap is to analyze data along the lines that he seems to have selected for himself, the conclusions that he might arrive at can be no stronger than the experimental data upon which those conclusions are based, and, therefore, for purposes of that kind of analysis, it would certainly be desirable to have the experimental data, in other words, the constitutional diagram, upon an absolutely firm basis.

Author's Closure

After this paper was prepared, a considerable improvement in the apparatus, and method of analysis was obtained. The furnace used at the present time appears as indicated in Fig. 1A. Samples are placed in the horizontal tube. After the crucible "O" is preheated and deoxidized, one of the samples from the horizontal tube is moved with a strong magnet, and dropped into the crucible. Gases evolved by this sample are collected and analyzed, as previously described. The furnace is supplied from a high frequency oscillator, and much higher temperatures than before (up to 1800 degrees Cent.) can be obtained and maintained.

Due to this improved practice much more satisfactory results were obtained in attempting to reduce different oxides. Experiments described on page 75 of the paper were repeated at higher temperatures, but even so only partial reduction could be obtained. SiO_2 as well as Al_2O_3 , passing through 200 mesh, would form fused globules which would float on the surface of molten charge in the graphite crucible. Consequently, reduction was very slow and only 31 per cent of SiO_2 , and 27 per cent of Al_2O_3 were reduced in 50 minutes. Buttons formed by these globules were taken out of the crucible and examined. They were nearly spherical in shape, glassy and almost transparent.

If, however, the same experiments were repeated, mixing powdered SiO_2 , and Al_2O_3 with about 10-20 per cent by weight of powdered graphite, formation of globules is prevented, and reduction takes place 90-95 per cent in 15



minutes for SiO_2 , and 91 per cent in 15 minutes for Al_2O_3 . Since this condition approaches one in which oxides are present in iron and steels, we feel justified to conclude that reduction of SiO_2 and Al_2O_3 inclusions by vacuum fusion method is complete within experimental error.

The above answers Dr. Hessenbruch's and Dr. Fitterer's remarks in regard to the method of analysis. To prevent throwing out small particles of oxides, power is shut off, and crucible cooled down, previously to introducing a sample, so that the latter lands on the surface of solidified iron. This is the practice used by Dr. Thanhuser at Düsseldorf. Besides, the crucibles are about 5 inches long, which is sufficient to keep all the samples inside.

Mr. Yap brought up several interesting points, and his thermodynamic treatment of our results is a valuable addition to the paper. The suggested existence of "metastable alpha iron" at temperatures over 1000 degrees Cent. (1830 degrees Fahr.) occurred to me as a possible explanation of points in Fig. 3 being so much scattered. However, a retrograde solubility may be correct, if the suggestion of a "peritectoid" reaction in iron-oxygen series is

correct (Fig. 2A). It is the line a-b-c-d that present experiments were attempted to determine.

I cannot agree with Mr. Yap's and Dr. Wasmuht's remarks in regard to FeO being in solid solution in iron. The fundamental property of solid solution is that the solute can diffuse through the solvent. Present experiments indicate clearly enough, it is hoped, that oxygen can diffuse through iron. Were FeO all the time present as a chemical compound, it would be very difficult to conceive its molecules, which are very large compared to iron atoms, traveling through the iron lattice to a depth of about one inch in a comparatively short time.

The low figures obtained for solubility of oxygen in iron at temperatures less than 800 degrees Cent. (1470 degrees Fahr.) led Messrs. Hessenbruch, Wasmuht, Leiter, Mehl and Fitterer to suggest that equilibrium was not reached because of the low rate of diffusion of oxygen at these temperatures. This point may be a subject for further investigations, particularly in view of the results of Krings and Kempkens. Their conditions, however, were different and more complicated than the ones used in the present experiments, being restricted to a binary system (iron and oxygen). Krings and Kempkens used ternary (iron-oxygen-hydrogen) and, perhaps, quaternary system (iron-oxygen-hydrogen-carbon, providing that carbon content of their samples exceeded 0.01 per cent. Catalytic action of the third and fourth elements may explain the difference in the results. Schenk has demonstrated that with still different conditions iron can be saturated with oxygen to even much higher figures (0.8 per cent O_2) than those given by Krings and Kempkens.

It should again be emphasized that the present results are correct only for oxygen and iron with a total amount of foreign elements not exceeding 0.01 per cent. Figs. 4 and 5 show clearly enough that even a small increase in carbon completely changes the results; and with other elements present, such as silicon, sulphur, phosphorus, manganese, etc., the results would become altogether different. This is the reason why Dr. Grossmann could not obtain the same results with vacuum fused ingot iron. Total amount of impurities in his samples, according to his own figures, was at least 0.02 per cent, in addition to small amounts of sulphur, phosphorus, and silicon.

Suggestions by Messrs. Yap, Hessenbruch, Wasmuht, Mehl, Herty and Hoyt, that iron containing various amounts of other elements and oxygen in form of compound gases (such as CO and CO_2) should be tried in the same manner, are very appropriate and I hope to be able to work on it. It would also be desirable to make use of other methods of investigation in parallel with the chemical methods.

Mr. Küttner, in a private letter, brought up a point that there may be a certain absorption of nitrogen by iron samples during the periods of bringing them up to the temperature in the nitrogen atmosphere. To the best of our knowledge, molecular nitrogen does not react with iron. Only in the atomic or ionized states, as in nitriding or welding, does reaction between iron and nitrogen take place. All samples discussed in this paper were analyzed for nitrogen, but the results obtained were so small (less than experimental error) that it was not considered necessary to present or even mention them.

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